

# (12) UK Patent Application (19) GB (11) 2 328 436 (13) A

(43) Date of A Publication 24.02.1999

(21) Application No 9818019.3

(22) Date of Filing 18.08.1998

(30) Priority Data

(31) 19735829

(32) 18.08.1997

(33) DE

(71) Applicant(s)

**Basf Aktiengesellschaft**  
(Incorporated in the Federal Republic of Germany)  
D-67056, Ludwigshafen, Federal Republic of Germany

(72) Inventor(s)

**Peter Schuhmacher**  
**Frank Meyer**  
**Karl Siemensmeyer**

(74) Agent and/or Address for Service

**J Y & G W Johnson**  
**Kingsbourne House, 229-231 High Holborn, LONDON,**  
**WC1V 7DP, United Kingdom**

(51) INT CL<sup>6</sup>

**C07C 69/96 , C09K 19/20**

(52) UK CL (Edition Q )

**C2C CAA CYT C200 C220 C227 C30Y C358 C36Y C364**  
**C366 C368 C43X C624 C628 C638 C648 C65X C658**  
**C66X C662 C668 C699 C80Y C815 C821**  
**C4X X12**  
**U1S S1346 S1387 S1389 S1399**

(56) Documents Cited

**WO 97/00600 A1**  
**Chemical Abstracts 83:106737 and JP490045149B4**  
**Chemical Abstracts 82:178983 and JP490037352B4**  
**Chemical Abstracts 75:41754**

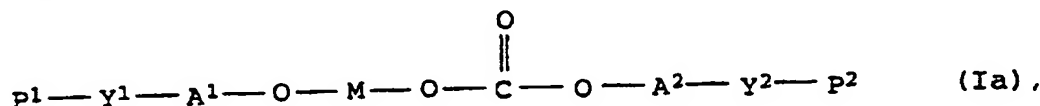
(58) Field of Search

**UK CL (Edition P ) C2C CYT , C4X**  
**INT CL<sup>6</sup> C07C 69/96 , C09K 19/20**  
**Online: WPI, CAS ONLINE**

(54) Abstract Title

**Liquid crystalline carbonic acid esters**

(57) Liquid-crystalline compounds have the formula Ia



where

$P^1$  and  $P^2$

each independently are hydrogen,  $C_1$ - $C_4$ -alkyl or reactive radicals by means of which polymerization can be brought about,

$Y^1$  and  $Y^2$

each independently are a single chemical bond, oxygen, sulfur, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -O-CO-NR-, -NR-CO-O- or -NR-CO-NR-,

R

$A^1$  and  $A^2$

is hydrogen or  $C_1$ - $C_4$ -alkyl,  
are spacers having one to 30 carbons in a chain which can be interrupted by oxygen in ether function, sulfur in thioether function or by nonadjacent imino or  $C_1$ - $C_4$ -alkylimino groups, and

M

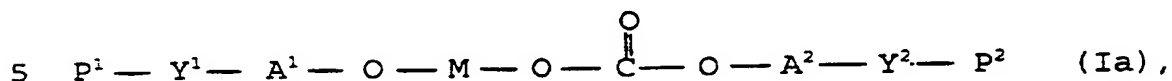
is a mesogenic group.

BEST AVAILABLE COPY

GB 2 328 436 A

Liquid-crystalline compounds

The present invention provides liquid-crystalline compounds of the formula Ia



where

$P^1$  and  $P^2$  each independently are hydrogen,  $C_1$ - $C_4$ -alkyl or reactive radicals by means of which polymerization can be brought about,

10  $Y^1$  and  $Y^2$  each independently are a single chemical bond, oxygen, sulfur,  $-O-CO-$ ,  $-CO-O-$ ,  $-O-CO-O-$ ,  $-CO-NR$ ,  $-NR-CO-$ ,  $-O-CO-NR$ ,  $-NR-CO-O-$  or  $-NR-CO-NR-$ ,

$R$  is hydrogen or  $C_1$ - $C_4$ -alkyl,

$A^1$  and  $A^2$  are spacers having one to 30 carbons in a chain  
15 which can be interrupted by oxygen in ether function, sulfur in thioether function or by nonadjacent imino or  $C_1$ - $C_4$ -alkylimino groups, and

$M$  is a mesogenic group.

The invention also provides mixtures which comprise  
20 compounds of the formula Ia, compositions which comprise compounds of the formula Ia with or without further additives, a process for preparing compounds of the formula Ia, processes for producing coatings from the novel compounds, mixtures or compositions, and articles  
25 coated by this process.

The invention provides, furthermore, for the use of the novel compounds, mixtures or compositions for preparing optical components and liquid-crystalline colorants, and it provides liquid-crystalline colorants and aqueous  
30 emulsions or dispersions which comprise the novel compounds, mixtures or compositions, and pigments which are obtainable by polymerizing the novel compounds, mixtures or compositions, the subsequent pigment size and form being established either before polymerization, by means

of appropriate techniques, or by comminution following polymerization.

The literature discloses numerous liquid-crystalline compounds that possess reactive (polymerizable) end groups. These end groups are separated by spacers from the mesogenic group M, the spacer generally being attached to M via an ether bond, as described, for example, in the documents EP-A 0648 827, EP-A 0611 981, EP-A 0739 403, WO 95/24454, WO 95/24455 or WO 86/24647. Examples of the attachment of the spacer to M via an ether bond as well as via a direct chemical bond are found in WO 95/22586. Liquid-crystalline compounds in which the spacer groups are attached to the mesogenic group M via carbonate units are noted in the document WO 97/00600.

In general, liquid-crystalline compounds with ether-bonded spacers (liquid-crystalline "ethers") are of lower viscosity than their counterparts with carbonate-bonded spacers (liquid-crystalline "carbonates"), which is generally desirable, and also have a greater tendency to form smooth, defect-free films, which is very important in view of the preparation of platelet-shaped particles of defined thickness, or use in coating materials. Moreover, ether attachment of the spacer to the mesogenic group M is chemically more stable than the carbonate attachment in relation, for example, to basic substances such as amines. An applicational disadvantage of the liquid-crystalline "ethers" relative to the "carbonates", however, is their generally lower liquid-crystalline phase width, which restricts the scope for their application.

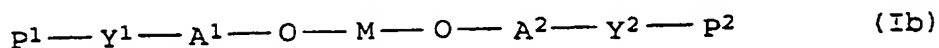
It is an object of the present invention, therefore, to provide liquid-crystalline compounds which combine the positive properties of the liquid-crystalline "ethers" and "carbonates" but without their negative properties. Furthermore, it should be possible to prepare these new liquid-crystalline compounds in a simple and hence cost-effective and time-saving manner.

We have found that this object is achieved by the compounds of the formula Ia described at the outset which can, furthermore, be prepared in a simple manner.

The invention additionally lays claim to mixtures comprising

(A<sub>1</sub>) one or more liquid-crystalline compounds of the formula Ia,

(A<sub>2</sub>) if desired, one or more liquid-crystalline compounds of the formula Ib

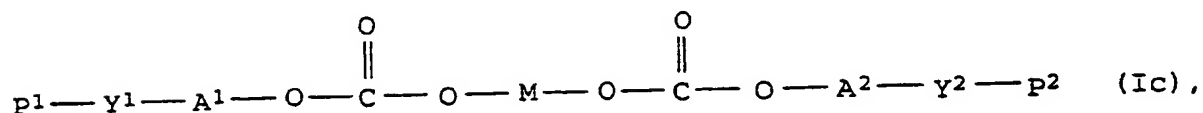


5

and/or

(A<sub>3</sub>) if desired, one or more liquid-crystalline compounds of the formula Ic

10



15

where p<sub>1</sub>, p<sub>2</sub>, y<sub>1</sub>, y<sub>2</sub>, A<sub>1</sub>, A<sub>2</sub> and M in the formulae Ib and Ic are each as defined in formula Ia but in specific individual cases their selection is independent for the compounds Ia, Ib and Ic.

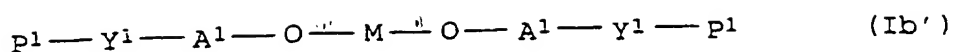
20 Such mixtures may therefore comprise component A<sub>1</sub> alone, a mixture of component A<sub>1</sub> and A<sub>2</sub> or of component A<sub>1</sub> and A<sub>3</sub> or a mixture of components A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub>. Compounds and mixtures of compounds which can be employed in accordance with the invention as component A<sub>2</sub> and whose structure is likewise that of formula Ib  
25 have been specified in the Preparation Examples of the documents WO 95/24454 and WO 95/24455 and in the Preparation Examples of the earlier German patent application 197 16 822.1. Express reference is made here to these compounds and their mixtures as a preferred component A<sub>2</sub>. In addition, the Preparation Examples of  
30 document WO 97/00600 set out compounds and mixtures of compounds which can be used in accordance with the invention as component A<sub>3</sub> and whose structure is that of the formula Ic. Consequently, express reference is made to these compounds and their mixtures  
35 as a preferred component A<sub>3</sub>.

Also claimed in accordance with the invention are mixtures comprising

40 (A<sub>1</sub>') one or more liquid-crystalline compounds of the formula Ia,

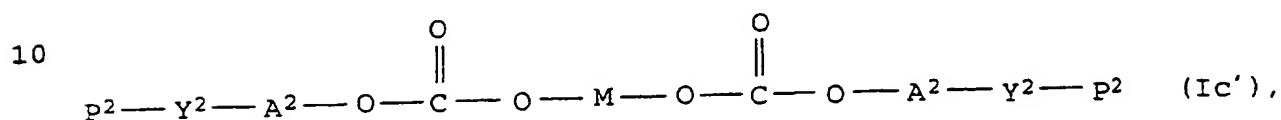
(A<sub>2</sub>') one or more liquid-crystalline compounds of the formula Ib'

45

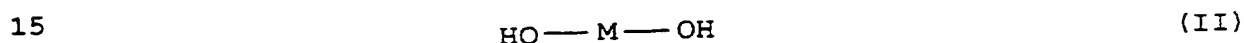


and

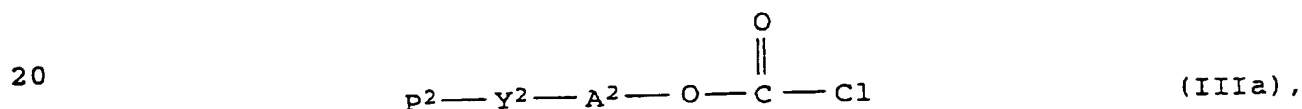
(A<sub>3</sub>') one or more liquid-crystalline compounds of the formula  
Ic'



obtainable by reacting one or more compounds of the formula II



with one or more compounds of the formulae IIIa and IIIb



25 where p<sup>1</sup>, p<sup>2</sup>, y<sup>1</sup>, y<sup>2</sup>, A<sup>1</sup>, A<sup>2</sup> and M are as defined above and Y<sup>3</sup> is a leaving group.

In contrast to the abovementioned mixtures comprising component A<sub>1</sub> and, if desired, components A<sub>2</sub> and/or A<sub>3</sub>, the preparation of these  
30 latter mixtures dictates a dependency between the variables of compounds of the formulae Ia, Ib' and Ic'.

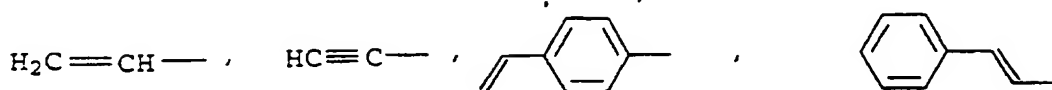
Moreover, the present invention also claims compositions  
35 comprising

(A) compounds of the formula Ia or mixtures comprising component A<sub>1</sub> alone or in a mixture with components A<sub>2</sub> and/or A<sub>3</sub>, or mixtures comprising components A<sub>1</sub>', A<sub>2</sub>' and  
40 A<sub>3</sub>', and

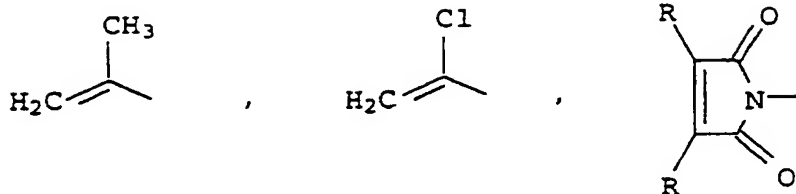
(B) further additives.

45 As reactive radicals p<sup>1</sup> and p<sup>2</sup>, by means of which polymerization can be brought about, it is possible in the novel compounds of the formula Ia and in the novel mixtures and compositions to use all radicals familiar to the skilled worker.

Among these, preferred reactive radicals P<sup>1</sup> and P<sup>2</sup> are



5



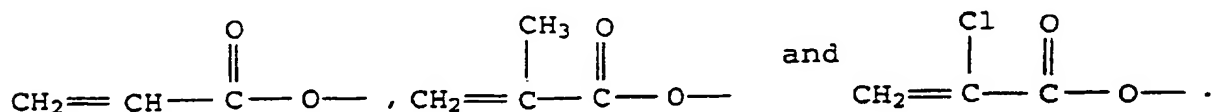
10

where R can be identical or different at each occurrence and is hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl.

15

Particularly preferred polymerizable groups P<sup>1</sup> and P<sup>2</sup> are those amenable to free-radical polymerization, and thus especially the olefinically unsaturated groups; among these, particularly important groups in combination with Y<sup>1</sup> or Y<sup>2</sup> are

20



25

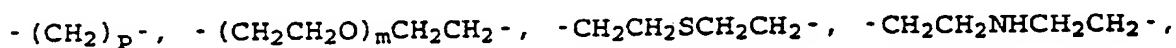
Unreactive radicals P<sup>1</sup> and P<sup>2</sup> employed can be hydrogen or C<sub>1</sub>-C<sub>4</sub>-alkyl such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl or t-butyl. These alkyls are also suitable both for the radicals R mentioned above in connection with the preferred reactive radicals P<sup>1</sup> and P<sup>2</sup> and in the definition of Y<sup>1</sup>

30

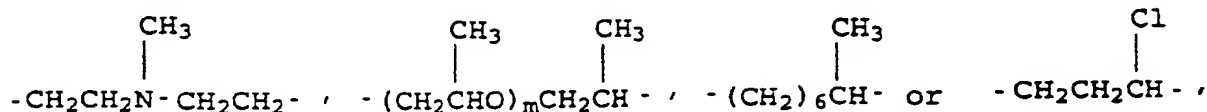
and Y<sup>2</sup>. Suitable spacers A<sup>1</sup> and A<sup>2</sup> are all groups known for this purpose. They contain 1 to 30, preferably 3 to 12 carbons and consist of predominantly linear aliphatic groups. They may be interrupted in the chain, for instance by nonadjacent oxygens, sulfurs, iminos or alkyliminos, such as methyliminos. Other suitable substituents of the spacer chain are fluorine, chlorine, bromine, cyano, methyl and ethyl.

35

40 Examples of representative spacers are:



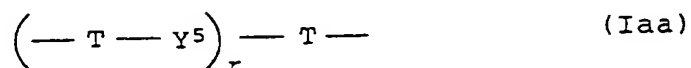
45



where

m is 1 to 3 and p is 1 to 12.

Appropriate radicals M are all known mesogenic groups, especially  
5 those of the formula Iaa



10 where:

T at each occurrence is a divalent, saturated or unsaturated,  
isocyclic or heterocyclic radical,

15 Y<sup>5</sup> at each occurrence is a group as defined for Y<sup>1</sup> and Y<sup>2</sup> or  
is -CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-, -CH=N-, -N=CH- or -N=N- and

r is 0, 1, 2 or 3,

20 and, if r > 0, both T and Y<sup>5</sup> are identical or different at each  
occurrence.

Preferably, r is 1 or 2.

25

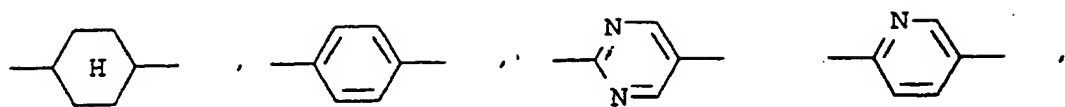
The radicals R may also carry up to three identical or different  
substituents from the following group:

hydrogen, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkoxycarbonyl,  
30 C<sub>1</sub>-C<sub>20</sub>-monoalkylaminocarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyl,  
C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyloxy, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonylamino, formyl,  
carboxyl, halogen, cyano, hydroxyl or nitro.

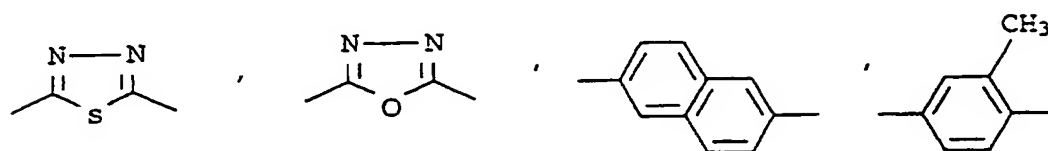
Preferred substituents of T other than fluorine, chlorine,  
35 bromine, cyano, formyl, carboxyl, nitro and hydroxyl are, in  
particular, short-chain aliphatic radicals such as methyl, ethyl,  
n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl and also  
alkoxys, alkoxycarbonyls, alkylcarbonyls, alkylcarbonyloxys,  
alkylcarbonylamino and monoalkylaminocarbonyls comprising said  
40 alkyls.

Examples of such radicals T are:

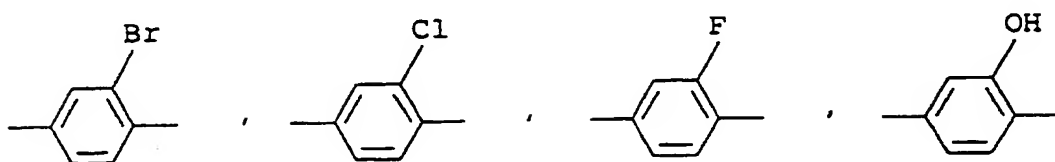
45



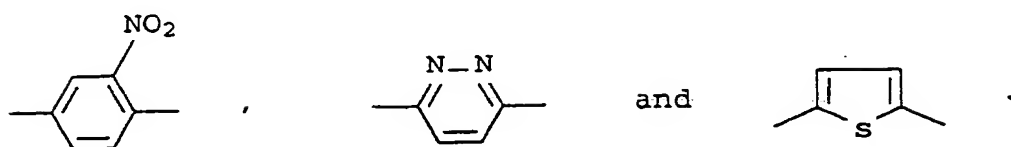
5



10

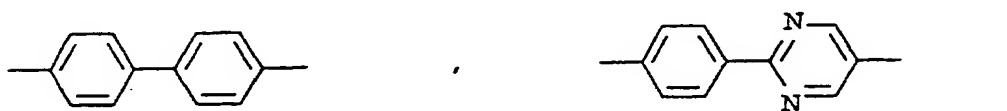


15

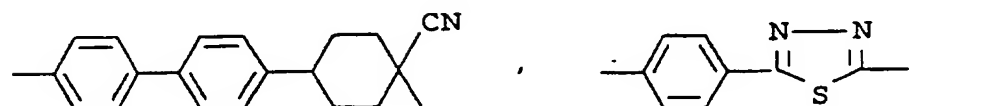


Examples of preferred mesogenic groups M are:

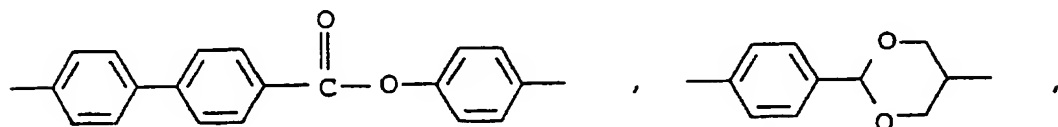
20



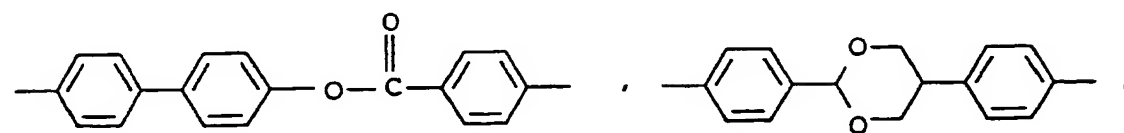
25



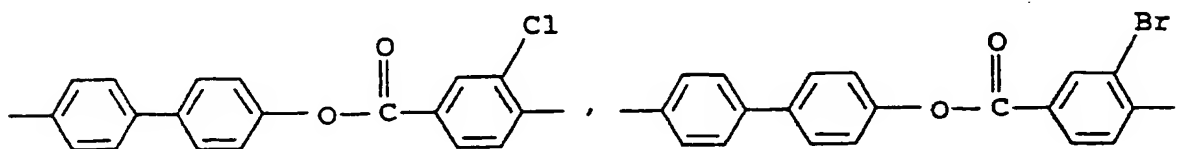
30



35

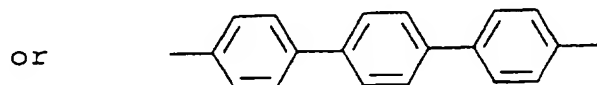
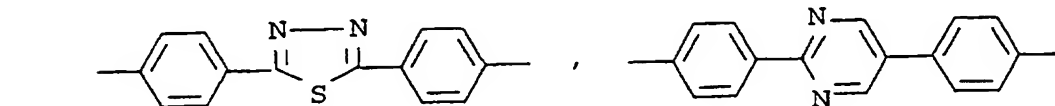
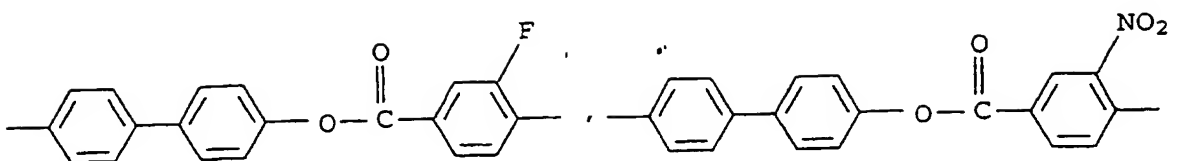


40

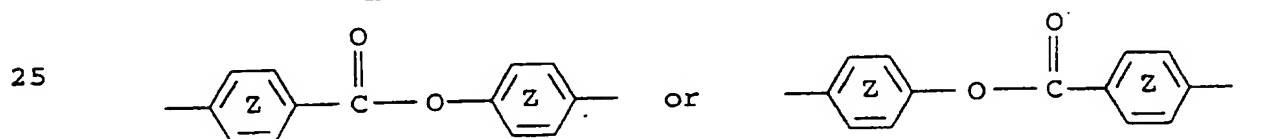
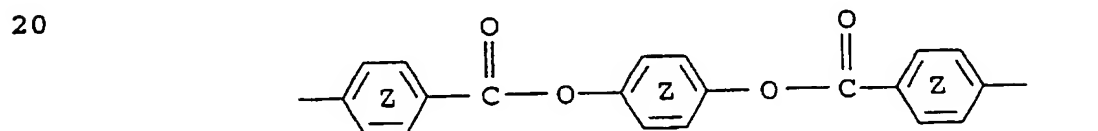
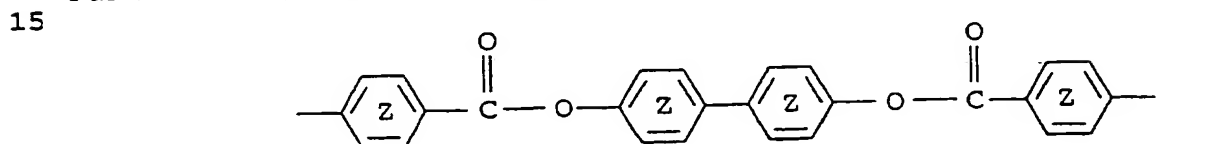


45





Particularly preferred mesogenic groups M are:

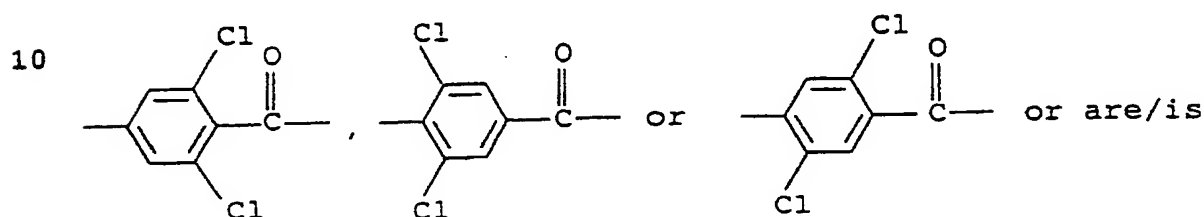
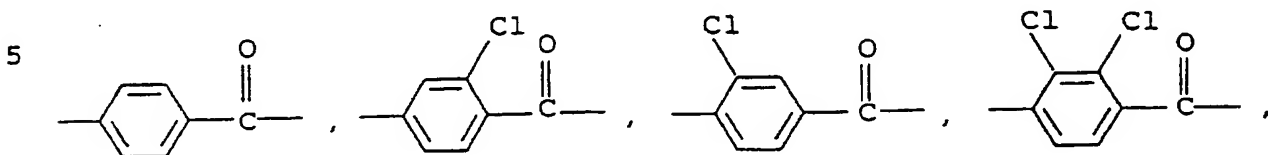


where each ring Z can carry up to three identical or different  
30 substituents from the following group:

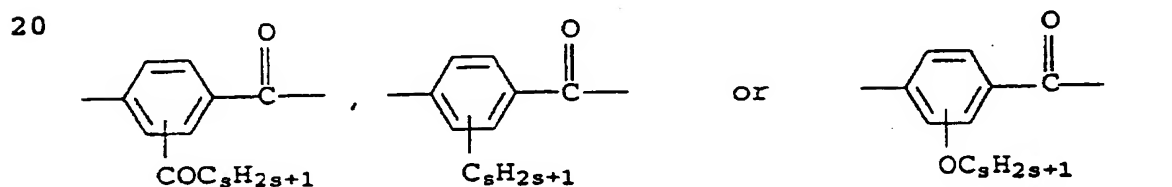
hydrogen, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkoxycarbonyl,  
C<sub>1</sub>-C<sub>20</sub>-monoalkylaminocarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyl,  
C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyloxy, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonylamino, formyl,  
35 carboxyl, halogen, cyano, hydroxyl or nitro.

Preferred substituents for the aromatic rings, other than  
fluorine, chlorine, bromine, cyano, formyl, carboxyl, nitro and  
hydroxyl are, in particular, short-chain aliphatic radicals such  
40 as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl  
and t-butyl and also alkoxys, alkoxycarbonyls, alkylcarbonyls,  
alkylcarbonyloxys, alkylcarbonylamino and  
monoalkylaminocarbonyls comprising said alkyls.

The outer benzene rings or, if only two are present, one benzene ring of the particularly preferred groups M have/has preferably the following substitution pattern:

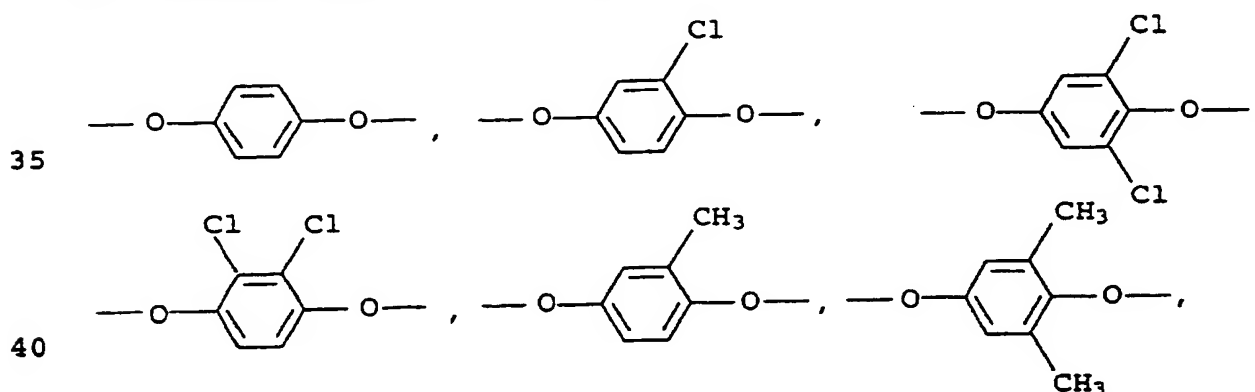


15 substituted similarly by F, Cl, Br, CH<sub>3</sub>, OCH<sub>3</sub>, CHO, COOH, COCH<sub>3</sub>, OCOCH<sub>3</sub> or CN instead of Cl, a mixture of substituents also being possible. Also to be mentioned are the structures

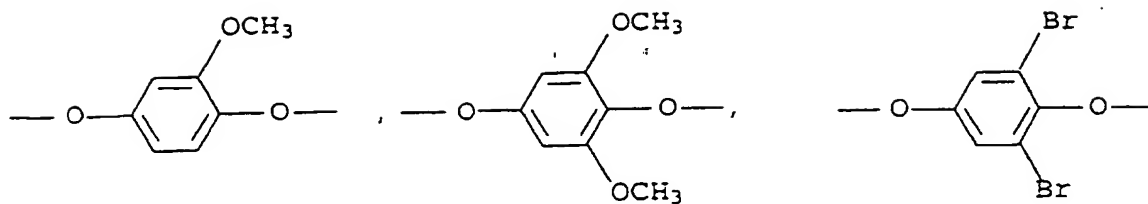


where s is 2 to 20, preferably 8 to 15.

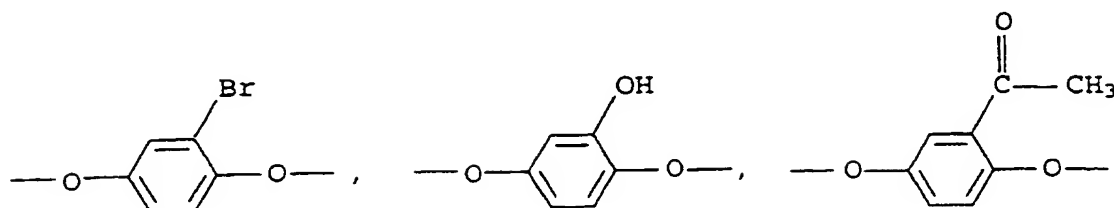
The preferred substitution patterns of the middle benzene ring, in the case of mesogenic groups M having three radicals T, of the particularly preferred groups M are



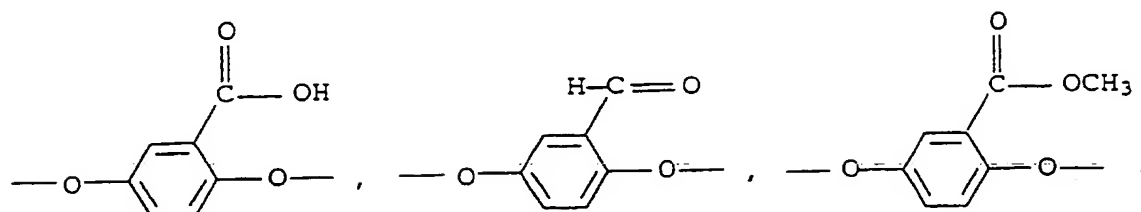
5



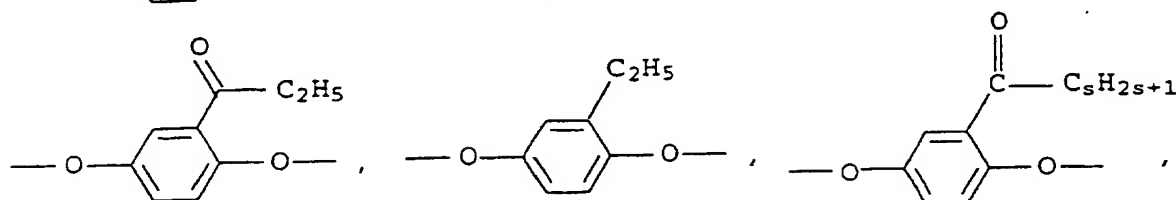
10



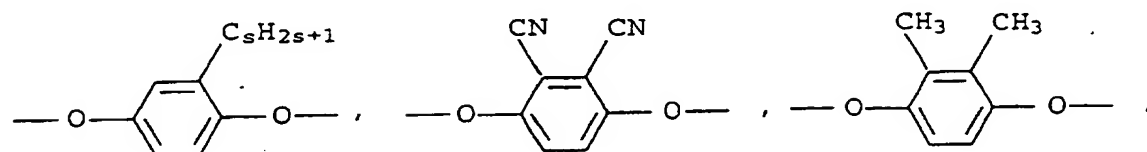
15



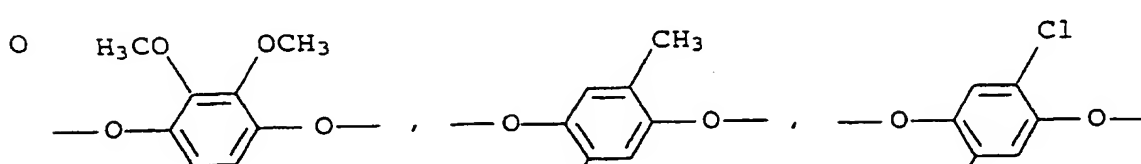
20



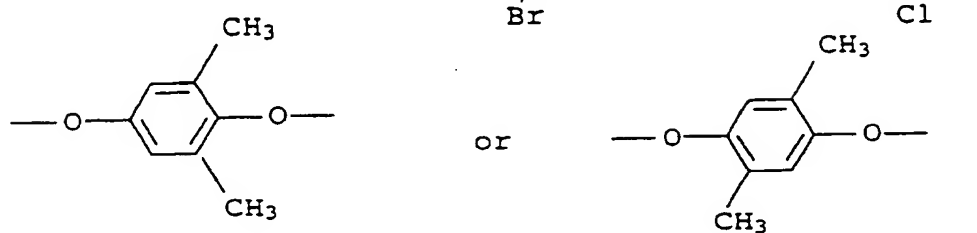
25



30



35



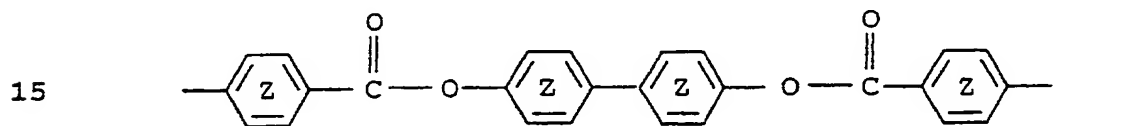
40

For technical applications, in the printing sector for example, it is often important to establish a desired viscosity.

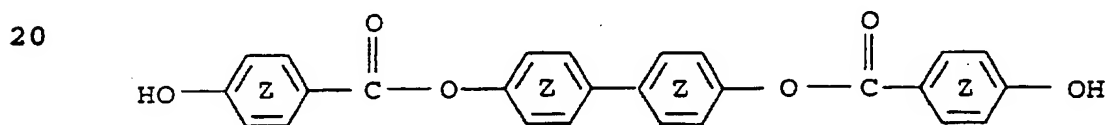
45

For this purpose it is therefore possible in the novel mixtures and compositions also to prepare mixtures of compounds of the formulae Ia, Ib, Ic or Ia, Ib', Ic' having different mesogenic groups M, inter alia. The viscosity of such mixtures is generally different from that of mixtures in which all compounds contain only one and the same mesogenic group M.

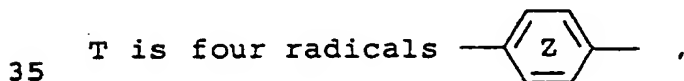
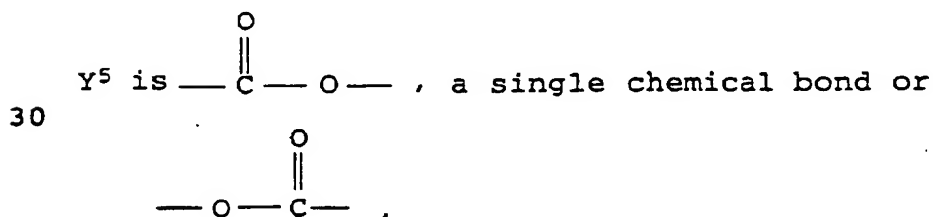
If it is intended, for example, to prepare mixtures comprising the components A<sub>1</sub>', A<sub>2</sub>' and A<sub>3</sub>' then it is possible for there to be not only, for example, "tetranuclear" mesogenic groups M, substituted or unsubstituted on the rings Z, of the formula



corresponding to a compound

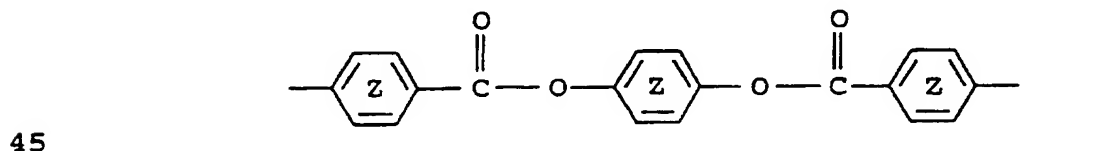


that is to be employed, or to the corresponding mono- or dianion, where in the formulae Ia, Ib' and Ic'

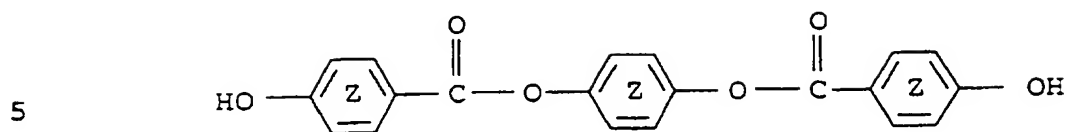


r is 3,

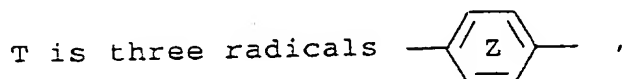
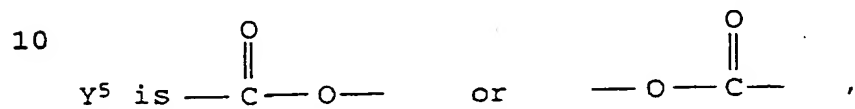
but also, for example, "trinuclear" mesogenic groups M, unsubstituted or substituted on the rings Z, of the formula



corresponding to a compound

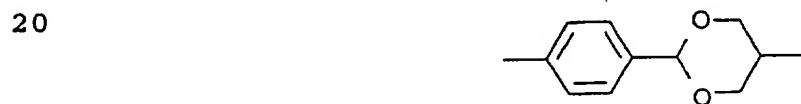


that is to be employed, or to the corresponding mono- or dianion, where in the formulae Ia, Ib' and Ic'

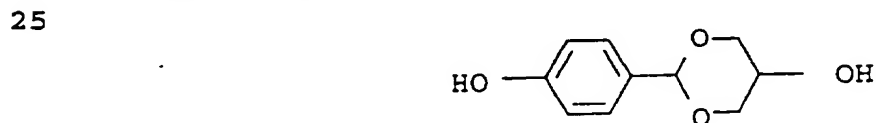


r is 2,

or else, for example, "dinuclear" groups M of the formula

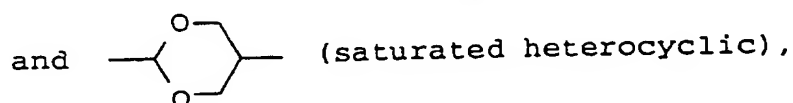
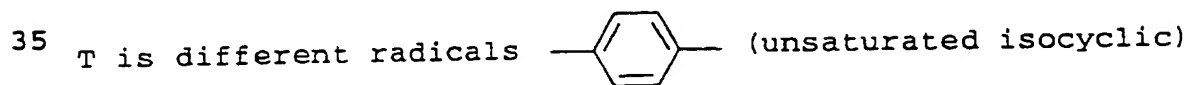


corresponding to a compound



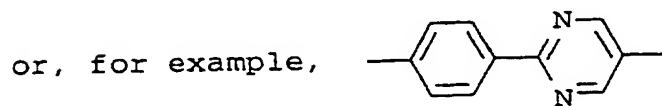
30 that is to be employed, or to the corresponding mono- or dianion, where in the formulae Ia, Ib' and Ic'

$Y^5$  is a single chemical bond,

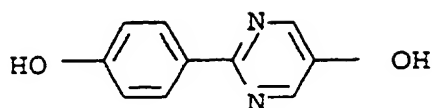


40

r is 1,



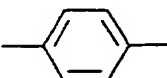
corresponding to a compound

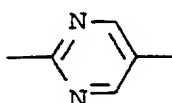


5

that is to be employed, or to the corresponding mono- or dianion, where in the formulae Ia, Ib' and Ic'

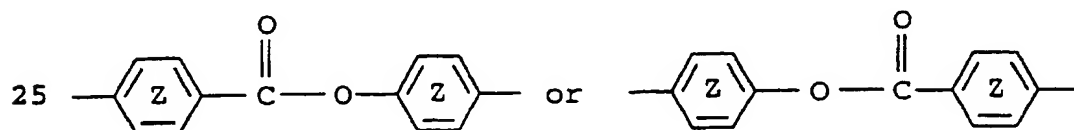
10  $Y^5$  is a single chemical bond,

T is different radicals  (unsaturated isocyclic)

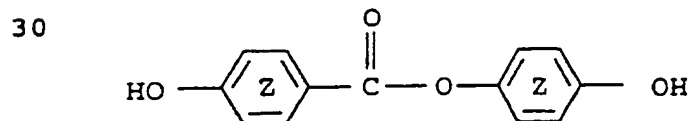
15 and  (unsaturated heterocyclic),

r: is 1.

20 Of these, particularly preferred "dinuclear" mesogenic groups M are the fragments



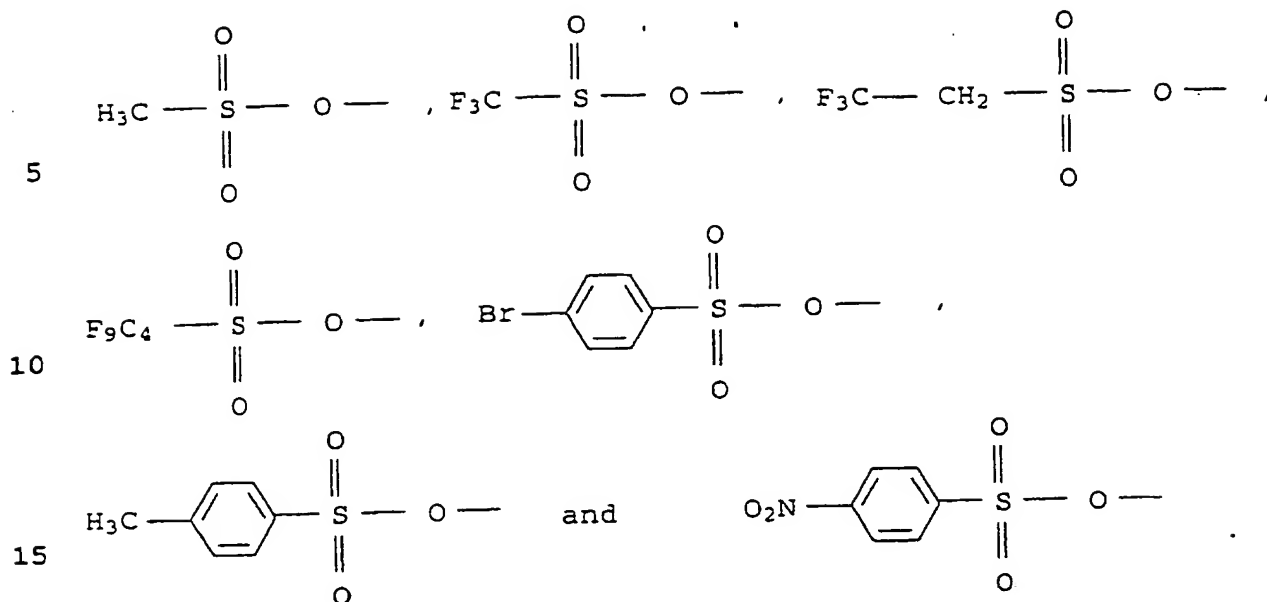
corresponding to the compound



35 that is to be employed, or to the corresponding mono- or dianion, which can additionally carry substituents on the aromatic rings Z, as described above.

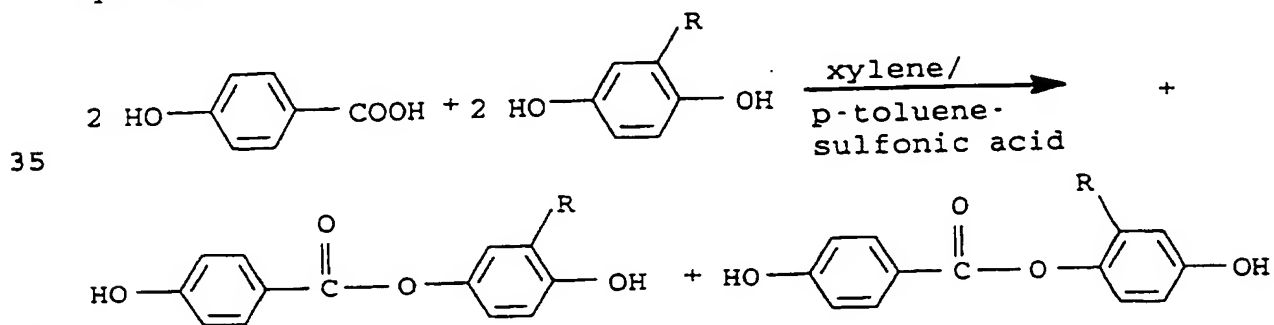
Groups which can function as leaving groups  $Y^{32}$ ,  $Y^{42}$  are all those  
40 known to the skilled worker. It is preferred here to employ halogens, especially Cl and Br. Preference is also given to the use of aliphatic or aromatic sulfonic acid derivatives and to aliphatic sulfonic acid derivatives substituted partly or completely by fluorine. Examples thereof are

45



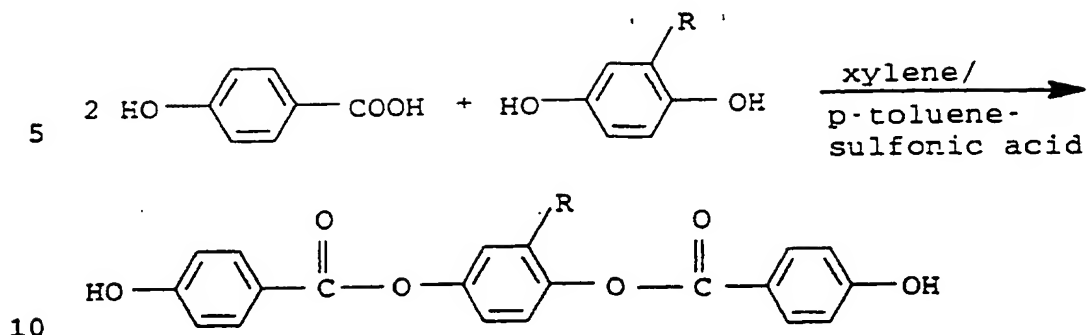
For the preparation of a mixture comprising the components  $A_1'$ ,  $A_2'$  and  $A_3'$ , use is advantageously made of mesogendiols whose mesogenic group M is of the formula Ia and where  $Y^5$  is  $-\text{COO}-$  or  $-\text{OOC}-$ . These mesogendiols are generally synthesized by azeotropic esterification. For example, as also known from the literature, it is possible from p-hydroxybenzoic acid and (substituted) hydroquinone, with addition of xylene as entrainer and p-toluenesulfonic acid as catalyst, to prepare, in accordance with the following equations and in dependence on the molar ratios employed, either a mixture of "dinuclear" mesogendiols (equation 1):

Equation 1:



or a "trinuclear" mesogendiol (equation 2):

Equation 2:



Each R here is as defined for the substituents of the above rings  
 Z of the particularly preferred mesogenic groups M. If R in  
 equation 1 is hydrogen, then the two resulting "dinuclear"  
 15 mesogendiols are of course chemically identical.

Entrainers which can be employed other than xylene are toluene  
 and other high-boiling aromatic compounds or else mixtures of  
 20 such hydrocarbons that are obtainable commercially, for instance  
 under the names Solvesso® or Aromatic®.

In addition to p-toluenesulfonic acid it is also possible to  
 employ the acids on which the preferred leaving groups Y<sup>3</sup>  
 25 described earlier are based, preferably in pure form or as a  
 concentrated aqueous solution. It is also possible with advantage  
 to use concentrated sulfuric acid, boric acid or a mixture of  
 these two acids.

30 The ratio of starting materials to entrainer is not critical;  
 usually, however, from about 200 to 350 µg of the entrainer are  
 employed per 100 g of starting materials.

35 The amount of catalyst employed is from about 1 to 10 g per 100 g  
 of starting materials employed, preferably from 1.5 to 4.5 g per  
 100 g of starting material.

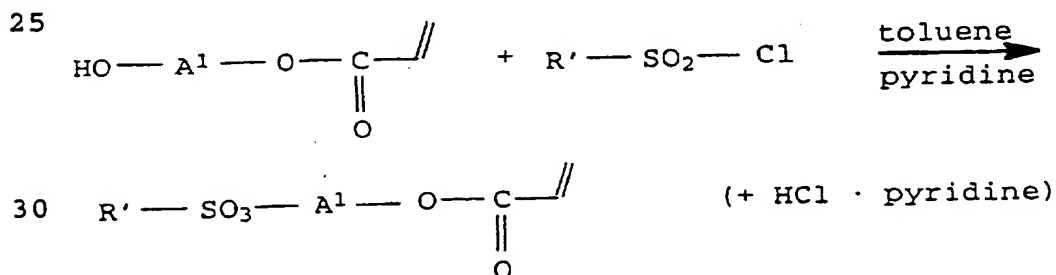
The reaction mixture, consisting of starting materials, entrainer  
 40 and catalyst, is rendered inert with nitrogen, heated and then  
 refluxed, during which the water is taken off completely as an  
 azeotropic mixture with the entrainer. The duration of the  
 reaction is normally from 4 to 12 hours. This time depends,  
 however, on the amounts and chemical nature of the starting  
 45 materials and entrainer employed and on the amounts and nature of  
 the acidic catalyst, and may therefore be longer or shorter in  
 specific cases. After the end of esterification the mixture is



cooled to room temperature and the crude crystalline product is filtered off with suction and washed with further entrainer or, if higher purities are desired, with solvents such as methanol or ethanol or mixtures thereof with water. Alternatively, the excess entrainer can also be separated off by steam distillation, with or without the addition of a customary commercial defoamer, and the solid product can be isolated from water by filtration. Similar syntheses of such mesogendiols have already been described elsewhere (for example Kongas et al., Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.) 30, pp. 462-463 (1989) and Müller et al., DE-A 36 22 611).

If the leaving groups  $Y^3$  of the compounds IIb that are used are sulfonate groups derived from aliphatic or aromatic unfluorinated, partly fluorinated or perfluorinated sulfonic acid derivatives, then to prepare the compounds IIb it is preferred to start from hydroxy compounds and from the acid chlorides of the sulfonic acid derivatives. The reaction below is intended to illustrate this taking as its example hydroxyalkyl acrylates (equation 3), of which many representatives are readily available commercially.

Equation 3:



$\text{R}'$  here is a radical derived, for example, from the sulfonate radicals already indicated earlier as preferred.  $\text{A}^1$  is as defined for formula IIb, and  $\cdot\text{Y}^1\text{-P}^1$  here is the group

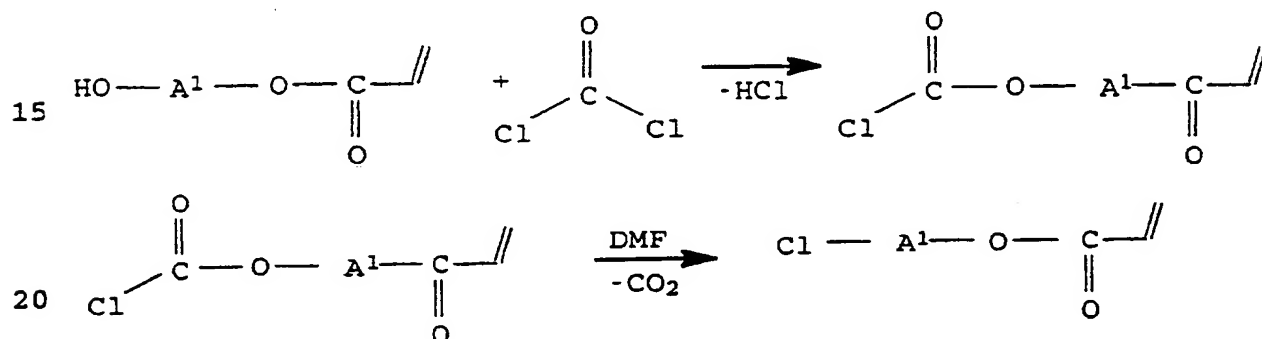


Toluene can also be replaced by other solvents, for example methylene chloride or ethers. Other than pyridine, suitable auxiliary bases are tertiary amines, such as N,N-dimethylcyclohexylamine, trimethylamine or triethylamine, and alkali metal or alkaline earth metal carbonates or bicarbonates,

the potassium salts preferably being employed here. Mixtures of such organic and inorganic bases can also be used.

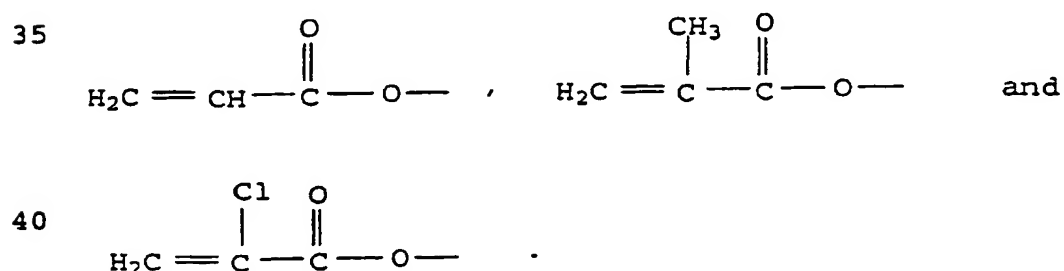
An elegant method to convert the OH group in hydroxyalkyl acrylates into chloride as the leaving group  $Y^3$  is to react the hydroxy compounds with phosgene, giving the intermediate chloroformates, which on addition of catalytic amounts of dimethylformamide give off  $CO_2$  to form the chloroalkyl acrylates (equation 4):

Equation 4:



Byproducts generally formed here in a proportion of less than 40 mol-% are also the corresponding compounds in which addition of the HCl onto the vinyl group of the acrylate radical has taken place. However, this does not cause further disruption, since in the course of the subsequent reaction hydrogen chloride is eliminated again with reformation of the vinyl group.

For reaction of the mesogendiols II to the novel compounds Ia or to the novel mixtures comprising the compounds Ia, Ib' and Ic' as components  $A_1'$ ,  $A_2'$  and  $A_3'$  it is particularly preferred to employ compounds IIIa and IIIb in which the reactive radicals  $P^1$  or  $P^2$ , form, together with the groups  $Y^1$  or  $Y^2$ , the following groups:



Here, the etherification of the mesogendiols II with the compounds IIIb takes place usually under the conditions of the Williamson ether synthesis. Bases preferably employed here are alkali metal and alkaline earth metal carbonates, particular

preference being given to the use of sodium, potassium and calcium carbonate. In the case of the preferred mesogendiols and of the particularly preferred co-reactants in which  $Y^5$  and also  $Y^1$  and  $Y^2$  are each correspondingly  $-COO-$  or  $-OOC-$ , the benzoic and acrylic ester groups present surprisingly remain intact, whereas when bases such as sodium or potassium hydroxide are used these groups are cleaved partially or totally depending, inter alia, on the amount of water and alkali.

To catalyze the etherification reaction it is possible to add alkali metal bromides or iodides and tetraalkylammonium bromides or iodides, preference being given in the former case to the use of potassium bromide or potassium iodide and in the latter case to the use of tetrabutylammonium bromide or tetrabutylammonium iodide.

Examples of suitable solvents are dimethylformamide, dimethylacetamide, N-methylpyrrolidone or else dimethyl sulfoxide; dimethylformamide is preferably employed.

The etherification generally takes place at from 70 to 110°C, and lasts usually from 4 to 24 hours, although in specific cases these ranges may be departed from at either end.

The etherification can advantageously also be conducted using chloroformates of the formula IIIa, since in the presence of dimethylformamide - whether as a solvent or in catalytic amounts in one of the abovementioned other solvents - spontaneous decarboxylation of these chloroformates takes place at the reaction temperatures indicated for the etherification (cf. also the second sub-equation of equation 4). In the final analysis the reactants present are compounds of the formula IIb where the leaving group  $Y^3$  is chlorine (or chloride). Consequently, what was said for the etherification in terms of bases, catalysts, solvents, reaction temperatures and durations applies equally in this case too.

If in reacting the mesogendiols of the formula II with compounds IIIa it is desired to retain the carbonate group, then it is normally necessary to operate at lower temperatures than in the case of etherification. In this case it is usual to operate at from 0 to 60°C, mostly in the range from 40 to 50°C. Depending on the reactivity of the co-reactants the reaction times are normally from 3 to 24 hours. Suitable solvents here are again those mentioned for the etherification, and dimethylformamide is again employed with preference. Although the latter also promotes

the decarboxylation reaction even at the lower temperatures, in this case the reaction with the mesogendiol or with the compound  $\text{HO-M-O-A}^2\text{-Y}^2\text{-P}^2$  obtained by the previous etherification step to give the target compound is kinetically favored. It is  
 5 advantageous, moreover, to conduct the etherification in the first step and the reaction with the chloroformates, at lower temperatures, in the subsequent step. If this sequence is reversed, cleavage and/or decarboxylation of the carbonate unit under the conditions of etherification can generally be expected,  
 10 although in certain cases even this procedure may lead to the desired products.

To scavenge the hydrogen chloride formed in the reaction with the chloroformate it is advantageous, before adding the  
 15 chloroformate, to add an auxiliary base in amounts at least equimolar to the chloroformate. Suitable such auxiliary bases are tertiary amines such as trimethyl-, triethyl- or else  $\text{N,N}$ -dimethylcyclohexylamine, pyridine or inorganic bases such as alkali metal or alkaline earth metal carbonates or bicarbonates,  
 20 and also mixtures of organic and inorganic bases.

Other bases which can be employed are alkali metal or alkali earth metal acetates. Preference is given to adding  
 25  $\text{N,N}$ -dimethylcyclohexylamine and potassium carbonate, either alone or in a mixture.

If in a first etherification step equimolar amounts of mesogendiol II and compound IIIb are employed then the generally  
 30 anticipated outcome is formation not only of the desired intermediate  $\text{HO-M-O-A}^1\text{-Y}^1\text{-P}^1$  but also of proportions of dietherified product  $\text{P-Y}^1\text{-A}^1\text{-O-M-O-A}^1\text{-Y}^1\text{-P}^1$  and of unreacted mesogendiol. To shift these proportions in favor of the intermediate it is possible with advantage to follow a procedure  
 35 in which, departing from the stoichiometric molar ratio of 1:1 for the proportion of mesogendiol to  $\text{P}^1\text{-Y}^1\text{-A}^1\text{-Y}^3$ , the diol is introduced in a solvent in a molar excess of from 2.5:1 to 10:1, preferably of 5:1. The compound IIIb is added to this initial charge and the excess, unreacted mesogendiol is removed with a  
 40 precipitant. After removing the solid by filtration the filtrate, containing the intermediate  $\text{P}^1\text{-Y}^1\text{-A}^1\text{-O-M-OH}$  which is readily soluble in both the solvent and the precipitant, is admixed in a second step with the chloroformate  $\text{P}^2\text{-Y}^2\text{-A}^2\text{-O-CO-Cl}$ . Customary work-up gives the pure target compound of the formula Ia or, in  
 45 the case of an asymmetric mesogenic group M or if two or more

mesogendiols are employed, a corresponding isomer mixture or a mixture of asymmetric compounds Ia".

5 In this case it is generally possible to employ, as solvents, the  
abovementioned compounds such as dimethylacetamide,  
N-methylpyrrolidone or dimethylformamide, for example, and, as  
precipitants, methanol, ethyl acetate, dichloromethane or butyl  
acetate, their action as solvents or precipitants depending of  
10 course on the solution properties of the mesogendiol and it being  
necessary for the intermediate to be readily soluble in the  
resulting mixture of solvent and precipitant. In each specific  
case, however, suitable solvents and precipitants can be found  
easily by experimentation.

15 If particularly pure products are desired, then it is  
advantageous to conduct the etherification reaction and the  
reaction with the chloroformates under an inert atmosphere, for  
example a nitrogen atmosphere. This makes it possible to prevent  
oxidative secondary reactions, especially on the mesogendiols.  
20

The addition of free-radical scavengers, such as commercially  
available nitroxyl compounds or else phenol derivatives, prevents  
premature polymerization of the target compounds when using  
25 compounds of the formulae IIIa and/or IIIb that contain acrylate  
groups, especially in the course of working up.

Whereas the activity of phenol derivatives is generally  
heightened in the presence of oxygen, nitroxyl compounds are  
30 effective even under an inert atmosphere, and for that reason are  
also preferably used in this case.

In preparing the mesogendiols it is also possible, of course and  
if desired, to operate under inert conditions. In this case the  
35 use of free-radical scavengers, although not necessary, can be  
practiced if the etherification reaction and the reaction with  
the chloroformates follow in a one-pot reaction. As already  
mentioned above, under inert conditions nitroxyl compounds will  
then preferably be added.  
40

In the case of relatively unreactive starting compounds of the  
formulae II and IIIb it may be sensible to work with two mutually  
immiscible liquids, for example water and methylene chloride. As  
45 the leaving group Y<sup>3</sup>, compound IIIb in this case preferably  
possesses a halogen, with particular preference Cl or Br, and is  
present almost exclusively in the organic phase. Where inorganic  
or strongly ionic organic bases are used, examples being

potassium carbonate or tetraalkylammonium hydroxides such as tetramethyl- or tetraethylammonium hydroxide, these are in contrast present almost exclusively in the aqueous phase. When the mesogendiol is added it is converted into its mono- or dianion, which although of only low solubility in the organic phase has a relatively high nucleophilicity, owing to its lower degree of solvation, and is therefore able to react with the halogen compound dissolved therein without having to compete with the base anion.

10

For working up, the reaction mixture is usually diluted with water and with an organic extractant having little if any miscibility with water, and the organic phase is washed a number of times with water and finally with aqueous mineral acid.

15

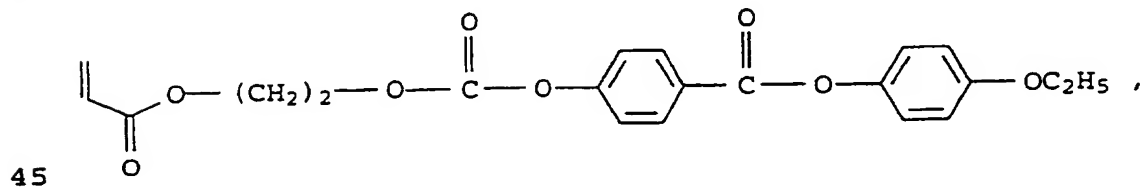
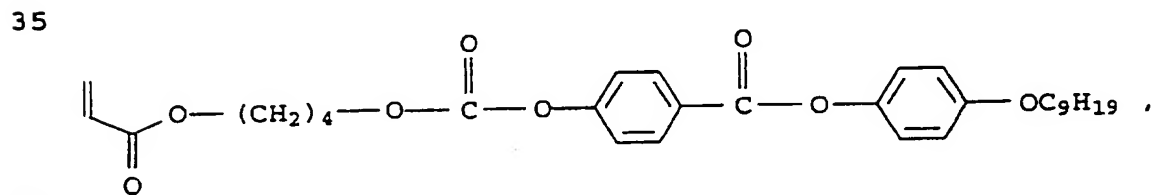
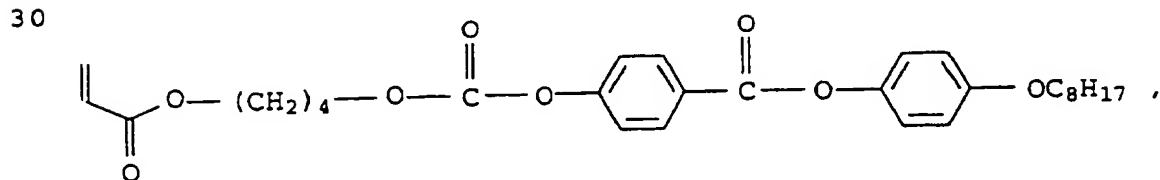
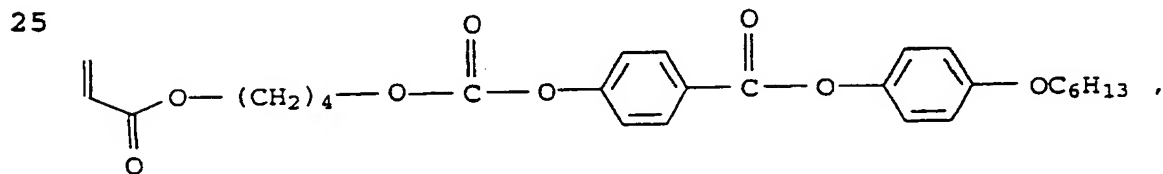
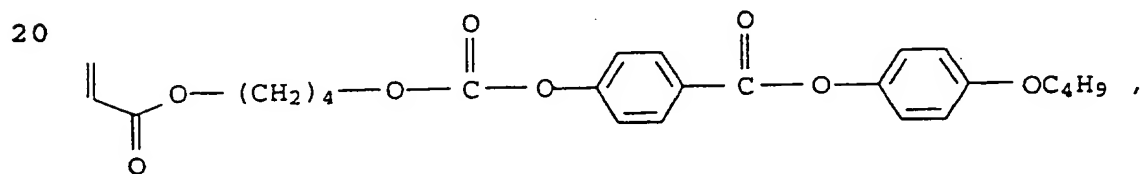
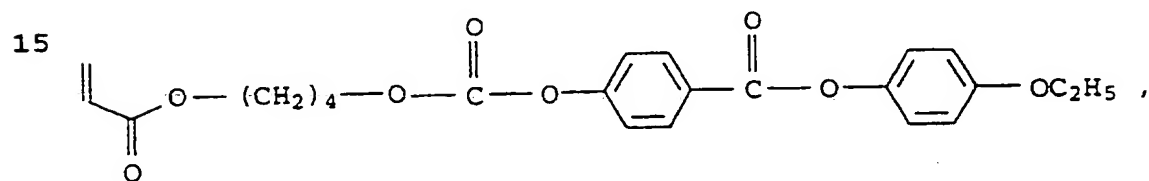
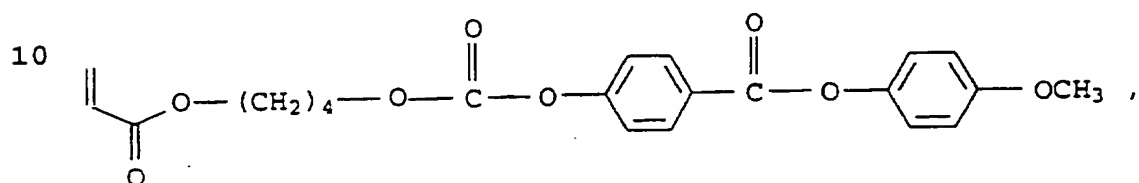
The organic extractant is removed by vacuum distillation at from 20 to 40°C. To prevent the premature polymerization of the product or products, distillative workup is preceded by the addition of customary inhibitors, such as methoxyphenol, Kerobit® BHT or phenothiazine, usually in a mixture, in amounts of from 0.01 to 1% by weight based on the product or products. The mixture of inhibitors varying in their volatility ensures adequate stabilization of the product or products in both the liquid and the vapor phases.

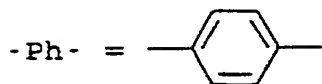
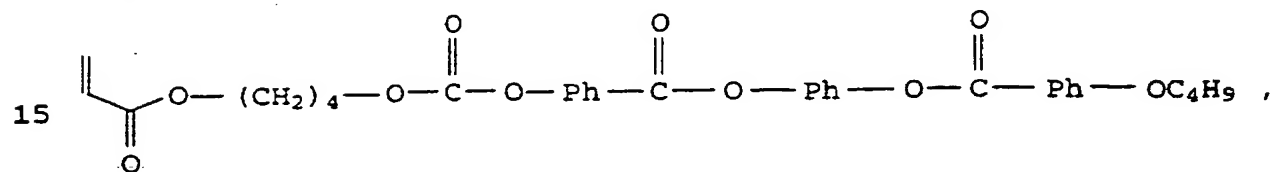
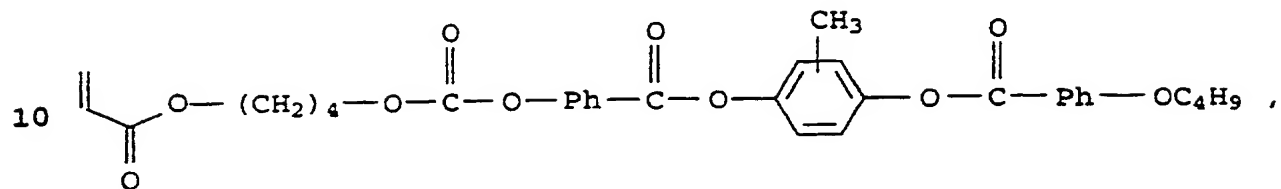
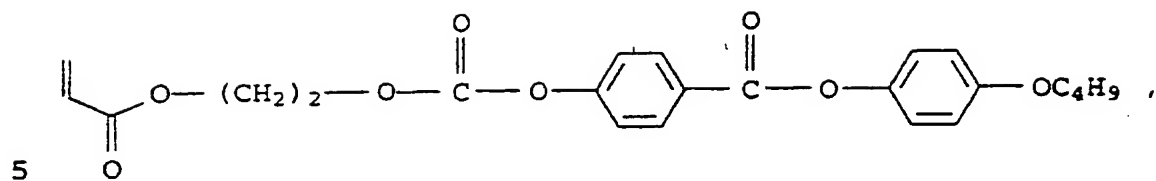
25

The novel compounds of the formula Ia can possess either two radicals  $P^1$  and  $P^2$  which are both unreactive, ie. are hydrogen or the abovementioned  $C_1$ - $C_4$ -alkyls; in these compounds one of  $P^1$  and  $P^2$  is unreactive and the other is reactive, or both radicals  $P^1$  and  $P^2$  are reactive. Also possible, furthermore, are mixtures of different compounds Ia in which doubly unreactive ( $P^1$  and  $P^2$  are unreactive), singly unreactive or singly reactive ( $P^1$  is unreactive and  $P^2$  is reactive or vice versa) and/or doubly reactive ( $P^1$  and  $P^2$  are reactive) compounds Ia are present. Preference is given to compounds Ia and mixtures of compounds Ia in which at least one of  $P^1$  and  $P^2$  is reactive or at least one compound Ia in the mixture of these compounds contains at least one reactive radical  $P^1$  or  $P^2$ . Preference is also given to novel mixtures (of components  $A_1$ ,  $A_2$  and  $A_3$  and of components  $A_1'$ ,  $A_2'$  and  $A_3'$ ), and novel compositions, in which at least one of  $P^1$  and  $P^2$  in at least one compound Ia is reactive.

Proportions of compounds Ia terminated at one or both ends by unreactive  $P^1$  or  $P^2$ , ie. by hydrogen or  $C_1$ - $C_4$ -alkyl, make it possible to adapt the properties of the novel mixtures or compositions, such as the liquid-crystalline phase width or

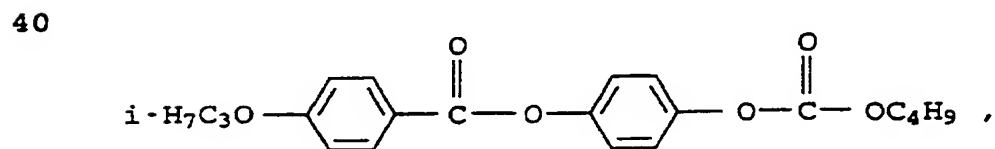
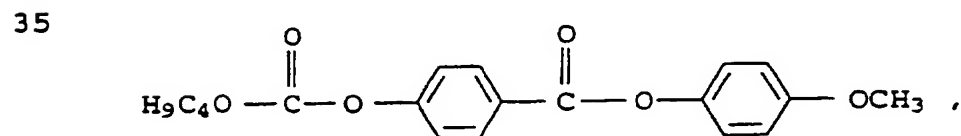
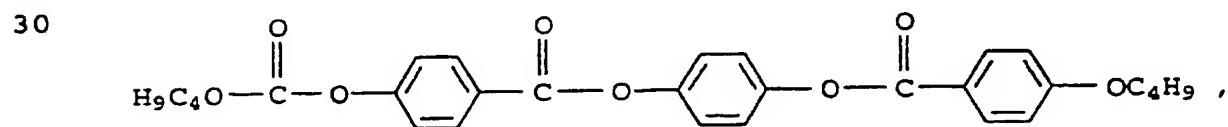
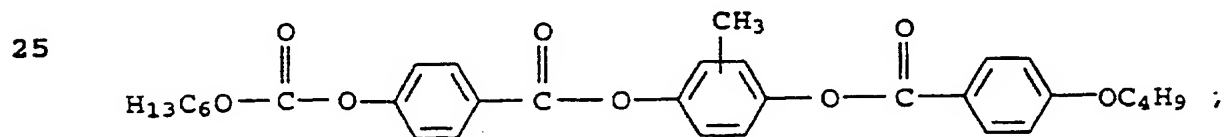
viscosity, to the particular requirements. By this means influence can also be had over the properties of polymers obtained from such mixtures or compositions. It is thus possible, for example, to vary their hardness, elasticity, glass transition temperature and permeability to liquids and gases on the basis of the altered degree of crosslinking. Examples of singly unreactive (or equivalent thereto singly reactive) compounds Ia are





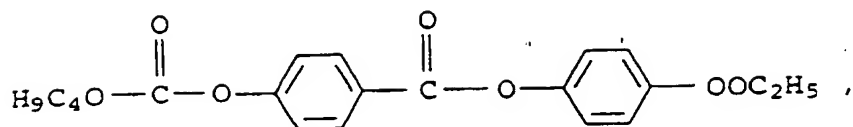
20

Examples of doubly unreactive compounds of the formula Ia are

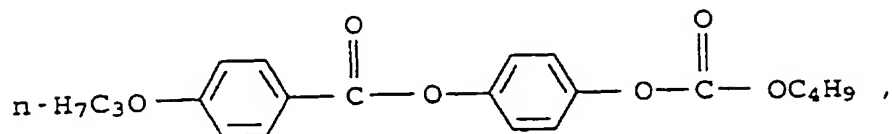


45

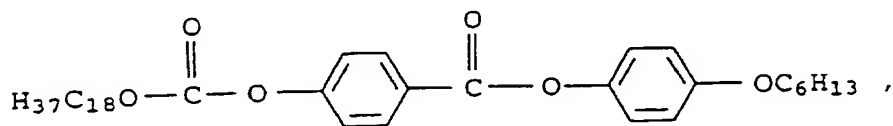




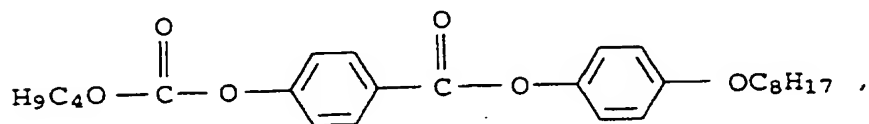
5



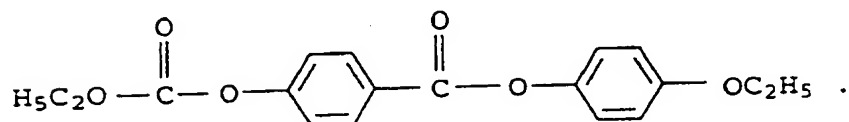
10



15



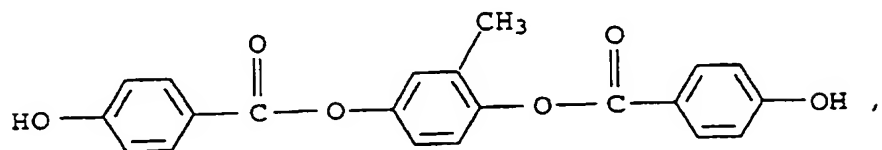
20



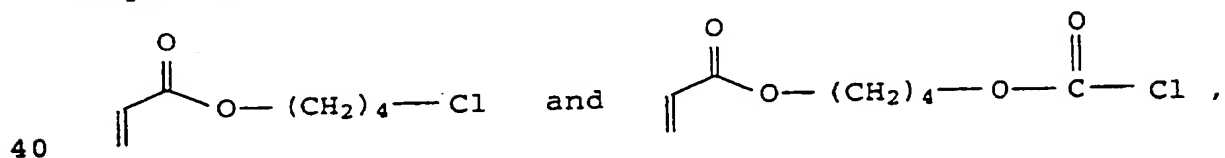
25

If the mesogendiol

30

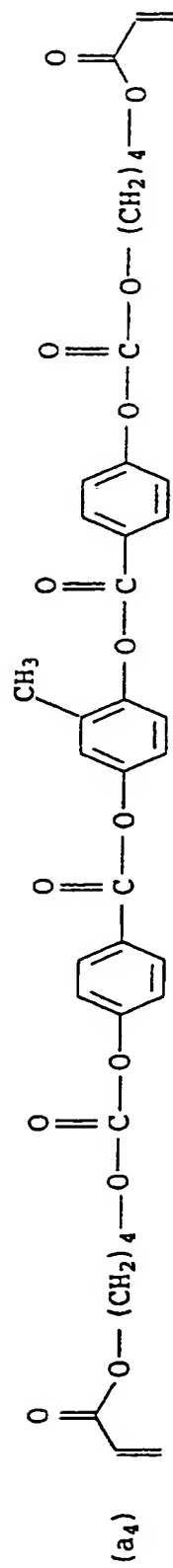
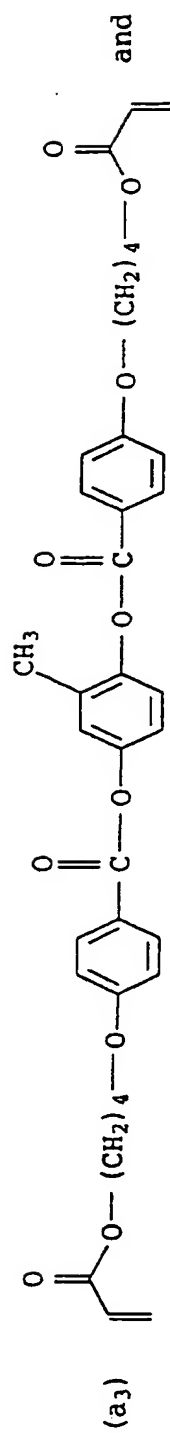
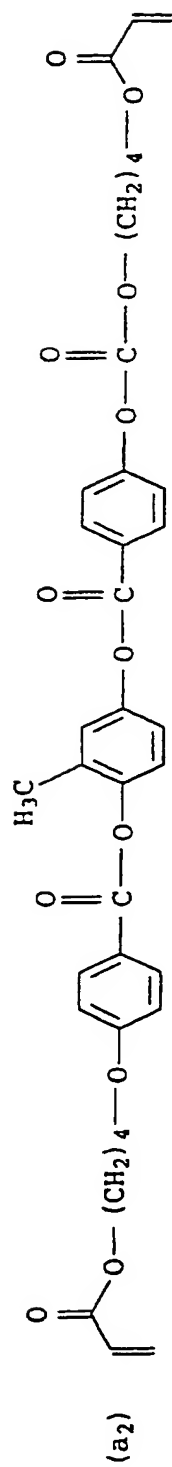
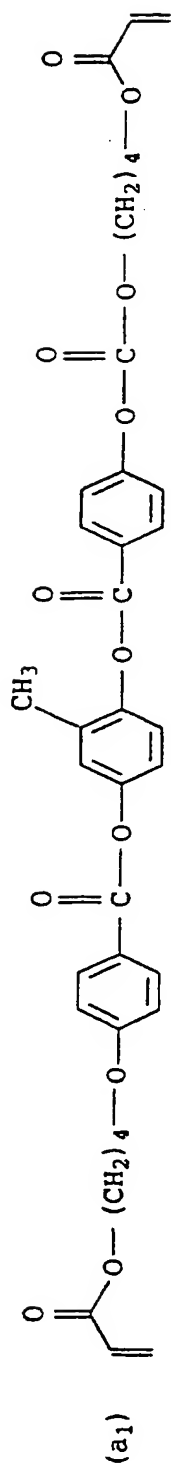


35 corresponding to a compound of formula II, is reacted with the compounds



40

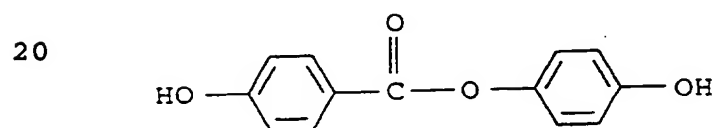
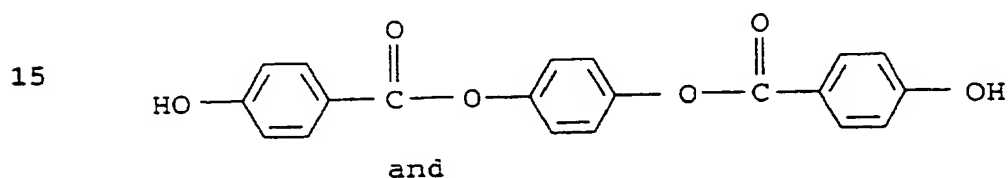
corresponding to compounds of the formulae IIb and IIa respectively, then the result is a mixture comprising compounds of the formulae  $a_1$ ,  $a_2$ ,  $a_3$  and  $a_4$  shown below. In this context, 45 the compounds of the formulae  $a_1$  and  $a_2$  shown below correspond to novel compounds Ia having two reactive radicals  $p^1$  and  $p^2$ .



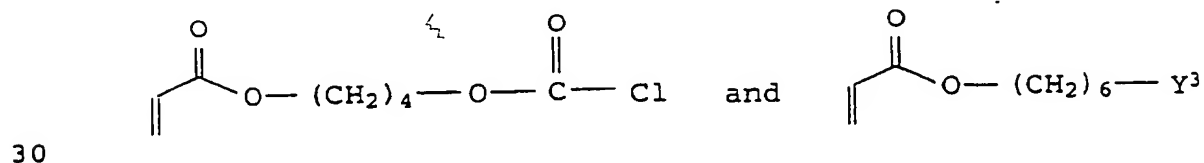
The compounds of the formulae  $a_1$  and  $a_2$  can be mentioned, moreover, as component  $A_1'$ , and the compounds of the formulae  $a_3$  and  $a_4$ , correspondingly, as components  $A_2'$  and  $A_3'$ , of mixtures obtainable in accordance with the invention.

Further details of the reaction of the mesogendiols of the formula II with compounds of the formulae IIIb and IIIa have already been given above.

If, for example, a mixture of the mesogendiols



is reacted with the compounds

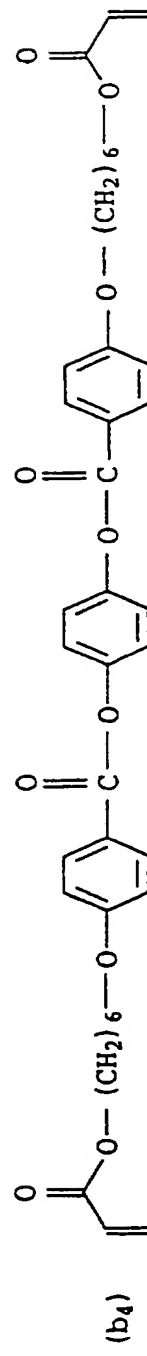
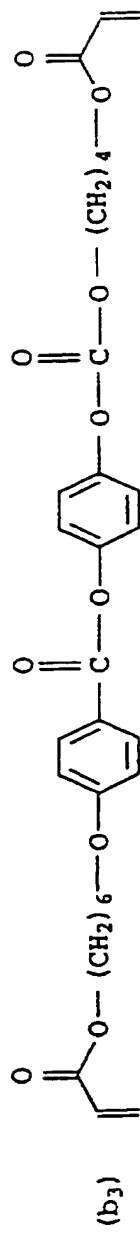
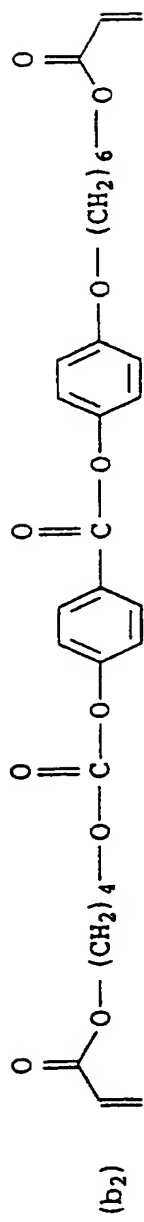
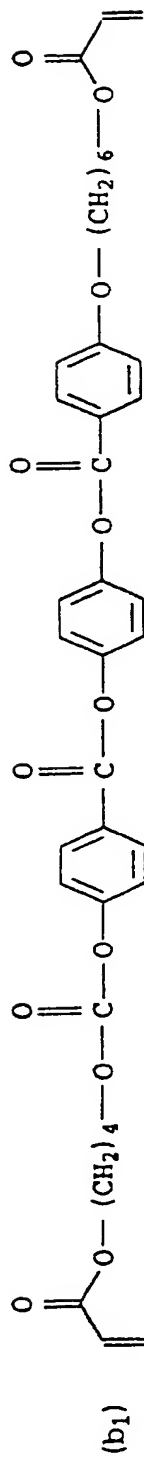


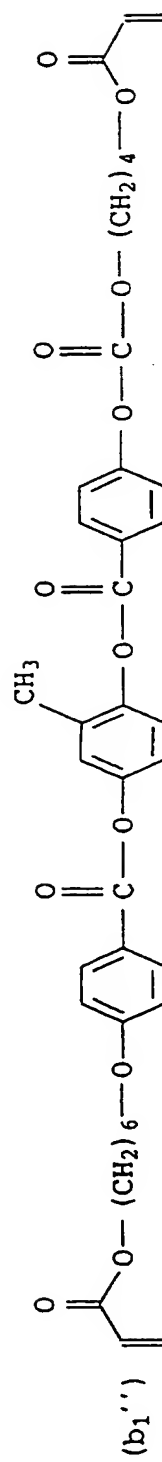
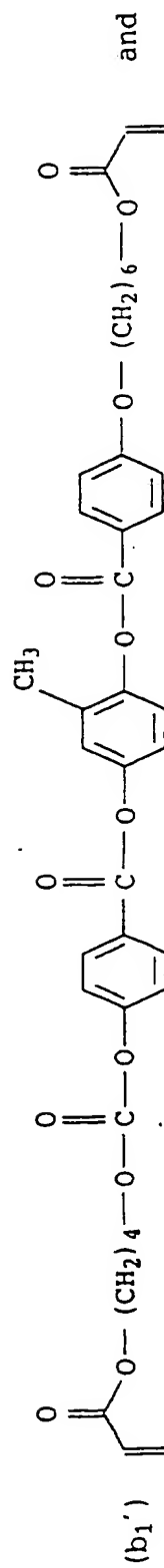
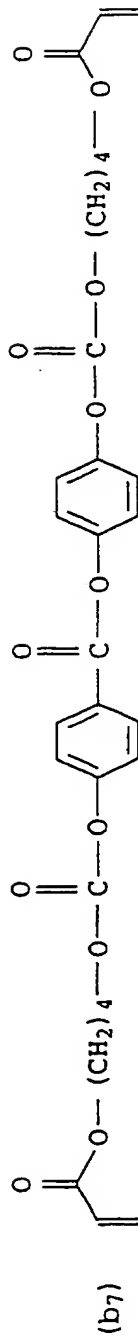
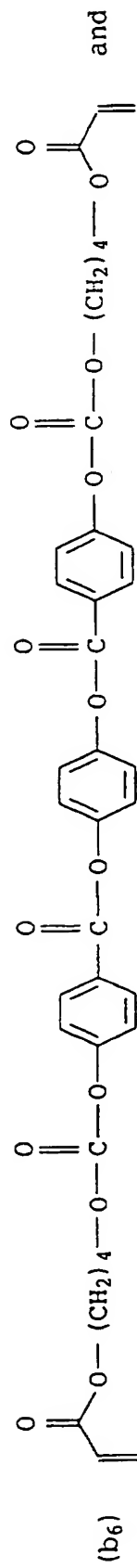
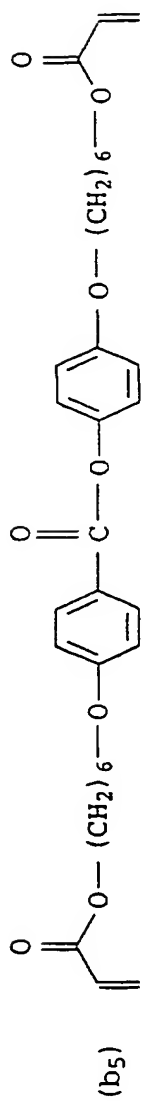
the result is a mixture comprising compounds of the formulae  $b_1$  to  $b_7$  shown below.

35

40

45





In this case, again, the compounds  $b_1$ ,  $b_2$  and  $b_3$  can be regarded both as examples of novel compounds of the formula Ia having two reactive radicals  $P^1$  and  $P^2$  and as constituents of the component  $A_1'$  of mixtures obtainable in accordance with the invention. The compounds  $b_4$  and  $b_5$  and, respectively,  $b_6$  and  $b_7$  are to be regarded, accordingly, as components  $A_2'$  or, respectively,  $A_3'$  of such mixtures. It should be noted here that owing to the asymmetric mesogenic unit the compounds  $b_2$  and  $b_3$  represent different chemical species. In the case of the compound  $b_1$  one would, on removing the symmetry of the mesogenic unit, for example by methyl substitution on the middle benzene ring of the mesogenic unit, likewise obtain two different compounds of the formulae  $b_1'$  and  $b_1''$  depicted above.

Aspects of the symmetry of mesogenic groups and the identity and nonidentity of liquid-crystalline compounds derived therefrom are dealt with exhaustively in the prior German patent application 197 16 822.1.

The compounds of components  $A_1'$ ,  $A_2'$  and  $A_3'$  specified in the two examples can of course be regarded as a specific selection, linked to one another by way of the preparation, of compounds of components  $A_1$ ,  $A_2$  and  $A_3$  of the novel mixtures.

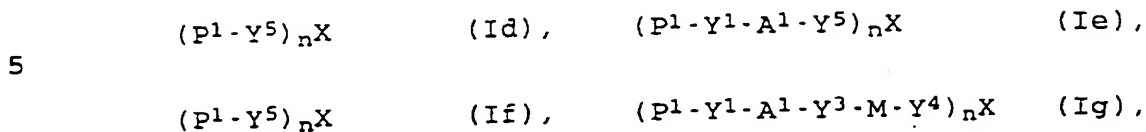
If further additives B are added to the novel compounds of the formula Ia or to the novel mixtures comprising the components  $A_1$ , optionally  $A_2$  and/or optionally  $A_3$  or the components  $A_1'$ ,  $A_2'$  and  $A_3'$ , this results in novel compositions.

Such additives B may be one or more chiral compounds.

In this way, cholesteric liquid-crystalline phases are formed which in particular have advantageous optical properties and which reflect light of different wavelengths depending, for example, on the viewing angle. Such liquid-crystal compositions find particular application as cholesteric liquid-crystalline colorants.

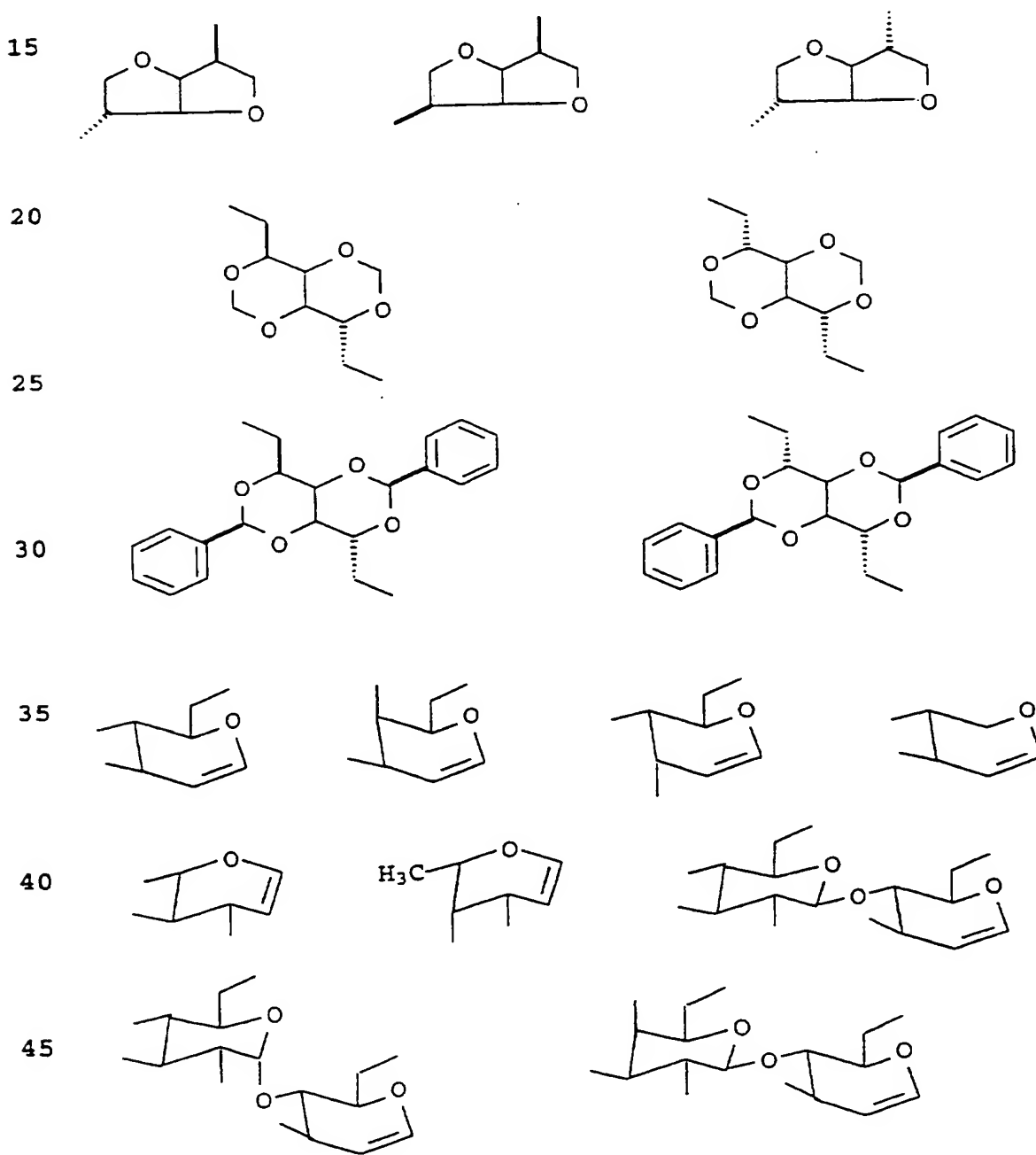
Particularly suitable chiral components are those which on the one hand have a high twisting capacity and on the other hand are readily miscible with the liquid-crystalline compounds, without disrupting the liquid-crystalline phase structure.

Examples of preferred chiral compounds are those of the formulae Id, Ie, If and Ig

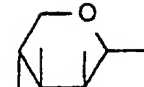
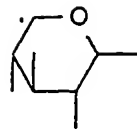
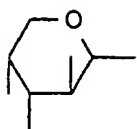
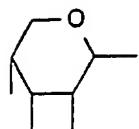


where  $P^1$ ,  $Y^1$ ,  $A^1$ ,  $Y^5$  and  $M$  are as defined for the formulae Ia and Iaa,  $n$  is an integer from 1 to 6,  $X$  is an  $n$ -valent chiral radical and  $Y^3$  and  $Y^4$  are as defined for  $Y^1$  and  $Y^2$ .

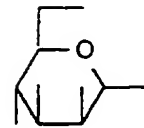
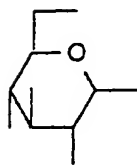
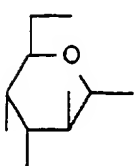
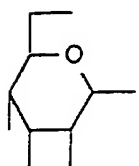
Examples of radicals  $X$  are:



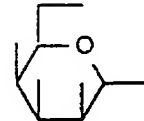
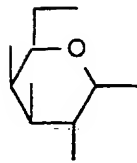
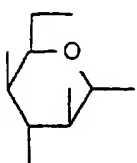
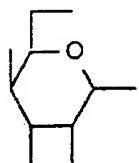
5



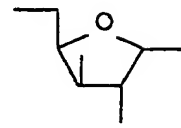
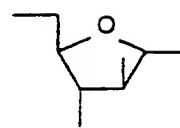
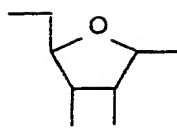
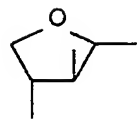
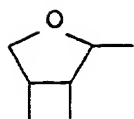
10



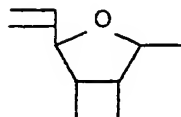
15



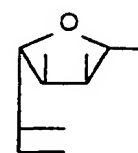
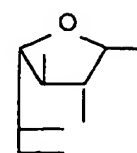
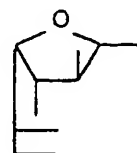
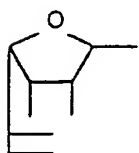
20



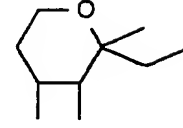
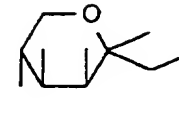
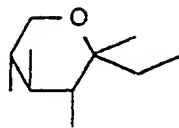
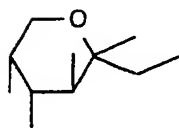
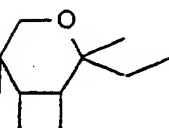
25



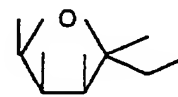
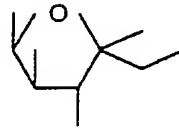
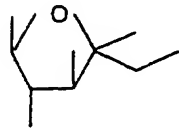
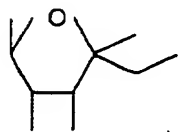
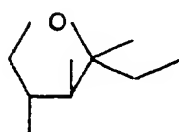
30



35



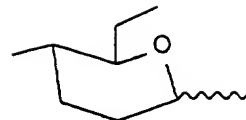
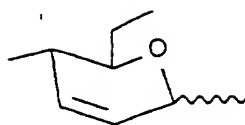
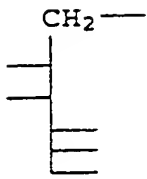
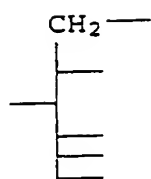
40



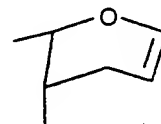
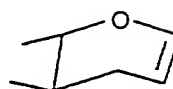
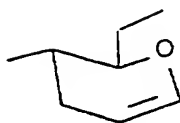
45



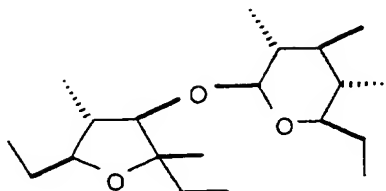
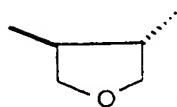
5



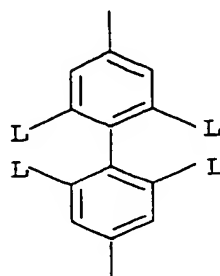
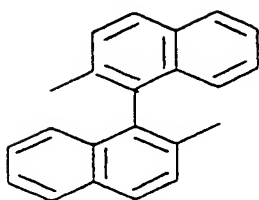
10



15



20



25

where

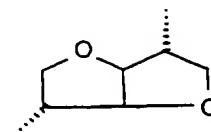
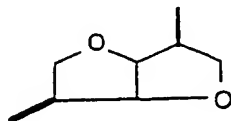
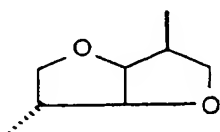
L is C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, halogen, COOR, OCOR, CONHR or NHCOR and R is C<sub>1</sub>-C<sub>4</sub>-alkyl.

30

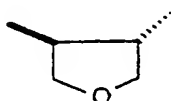
(The lines at the end in the given formulae indicate the free valences.)

Particular preference is given to

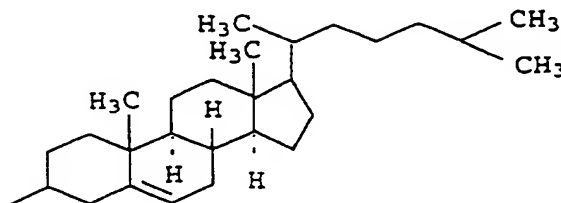
35



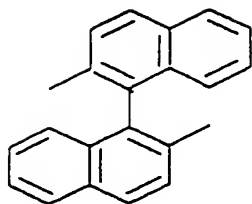
40



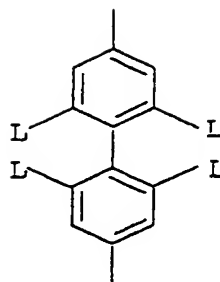
45



5



or



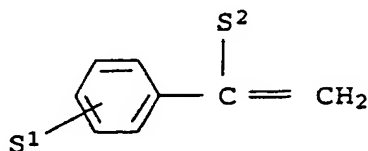
10 These and other chiral components are specified, for example, in the documents WO 95/16007, DE-A 1 95 20 660 and DE-A 1 95 20 704.

As further additives B it is also possible to add  
 15 liquid-crystalline compounds or mixtures thereof, as set out in the documents WO 95/22586, WO 95/24454, WO 95/24455, WO 96/30352 and WO 97/00600, or liquid-crystalline mixtures prepared by the method described in the document WO 96/04351.

20 Polymerization of the novel compounds, mixtures or compositions, which is of course only possible if at least one of P<sup>1</sup> and P<sup>2</sup> is reactive, makes it possible to fix the liquid-crystalline order state. Depending on the polymerizable group, polymerization may take place thermally or photochemically, for example. In this  
 25 context it is also possible to copolymerize other monomers together with the liquid-crystalline compounds or mixtures. These monomers, which are likewise - alone or in a mixture with other additives - to be regarded as additives B of the novel compositions, include customary crosslinkers. Examples of  
 30 suitable monomers are:

vinylaromatic compounds, such as styrene or styrene derivatives of the formula

35



40 where S<sup>1</sup> and S<sup>2</sup> are hydrogen or C<sub>1</sub>-C<sub>6</sub>-alkyl;

acrylonitrile, methacrylonitrile, cyanoacrylonitrile;

45 C<sub>1</sub>-C<sub>4</sub>-alkyl esters of acrylic acid, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and ethylhexyl acrylate and the corresponding methacrylates, and also

cyanoacrylic acid; and, in addition, the glycidyl esters, glycidyl acrylate and glycidyl methacrylate.

As crosslinkers (crosslinking monomers) it is possible to employ  
5 bi- or polyfunctional compounds having at least 2 olefinic double  
bonds, examples being divinyl esters of dicarboxylic acids such  
as of succinic and adipic acid, diallyl and divinyl ethers of  
bifunctional alcohols such as of ethylene glycol and of  
1,4-butanediol, methacrylic or acrylic esters of polyfunctional  
10 alcohols, especially those which other than the hydroxyls contain  
no further functional groups or, if any at all, then ether  
groups. Examples of such alcohols are bifunctional alcohols, such  
as ethylene glycol, propylene glycol and their counterparts with  
higher degrees of condensation, such as diethylene glycol,  
15 triethylene glycol, dipropylene glycol, tripropylene glycol,  
etc., butanediol, pentanediol, hexanediol, neopentyl glycol,  
alkoxylated phenolic compounds, such as ethoxylated and/or  
propoxylated bisphenols, cyclohexanedimethanol, alcohols of the  
functionality of three or more, such as glycerol,  
20 trimethylolpropane, butanetriol, trimethylolethane,  
pentaerythritol, ditrimethylolpropane, dipentaerythritol,  
sorbitol, mannitol and the corresponding alkoxylated alcohols,  
especially ethoxylated and propoxylated alcohols.

25 Also suitable are polyester (meth)acrylates, which are the  
(meth)acrylic esters of polyesterols.

Examples of suitable polyesterols are those as can be prepared by  
30 esterifying polycarboxylic acids, preferably dicarboxylic acids,  
with polyols, preferably diols. The starting materials of such  
hydroxyl-containing polyesters are known to the skilled worker.  
Dicarboxylic acids that can be employed are succinic, glutaric,  
adipic, sebacic and o-phthalic acid, their isomers and  
35 hydrogenation products, and esterifiable derivatives, such as  
anhydrides or dialkyl esters, of these acids. Suitable polyols  
are the abovementioned alcohols, preferably ethylene glycol, 1,2-  
and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol,  
neopentyl glycol, cyclohexanedimethanol and also polyglycols of  
40 the ethylene glycol and propylene glycol type.

The crosslinkers (crosslinking monomers) may also comprise, for  
example, epoxy or urethane (meth)acrylates.

Epoxy (meth)acrylates are those, for example, as obtainable by the reaction, familiar to the skilled worker, of epoxidized olefins or of poly- or diglycidyl ethers, such as bisphenol A diglycidyl ether, with (meth)acrylic acid.

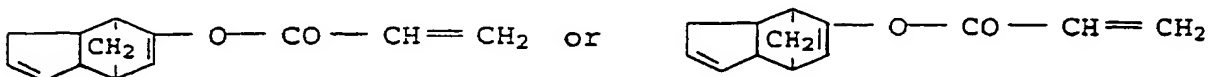
5

In the case of urethane (meth)acrylates the compounds involved are again known to the skilled worker and are reaction products of hydroxyalkyl (meth)acrylates with poly- and/or diisocyanates.

10

Further suitable crosslinkers (crosslinking monomers) are 1,4-divinylbenzene, triallyl cyanurate, acrylic esters of tricyclodecenyyl alcohol of the following formula

15



known under the name of dihydrodicyclopentadienyl acrylate, and  
the allyl esters of acrylic, methacrylic and cyanoacrylic acid.

If monomers and/or crosslinkers (crosslinking monomers) are employed then their amount must be adapted to the polymerization conditions firstly so as to give a satisfactory, desired effect and secondly so that the liquid-crystalline phase behavior is not too adversely affected. The amount of the optional monomers and/or crosslinkers to be employed depends in general on the use of the polymers. To prepare pigments, a relatively large amount and, to prepare thermoplastic coatings, a relatively small amount of monomers/crosslinkers may be advantageous. The amount of the monomers/crosslinkers can generally be determined by means of a few preliminary experiments. Normally, however, an attempt will be made to keep the proportion of monomers/crosslinkers (crosslinking monomers) low or to use none at all.

35

Further additives (B) can be polymeric auxiliaries, such as leveling assistants, defoamers, devolatilizing agents, rheological assistants or adhesion promoters. Such auxiliaries should preferably be soluble either in the initial mixtures or in an organic solvent compatible with the initial mixtures. Typical examples of such polymer auxiliaries are polyesters, cellulose esters, polyurethanes and also unmodified, polyether-modified or polyester-modified silicones. The amount of polymer auxiliary to be added, if at all, for the desired purpose, its chemical nature, and possibly the amount and type of solvent as well are

45

generally familiar to the skilled worker or can likewise be determined experimentally by means of a few preliminary trials.

If the compositions of the invention are subjected to a photochemical polymerization, then further possible additives are photoinitiators. Examples of these are the substances available commercially under the tradenames Lucirin<sup>®</sup>, Irgacure<sup>®</sup> and Darocure<sup>®</sup>, for instance Lucirin<sup>®</sup> TPO, Irgacure<sup>®</sup> 184, Irgacure<sup>®</sup> 369, Irgacure<sup>®</sup> 907 and Darocure<sup>®</sup> 1173. In this case the initiators are employed in customary amounts, corresponding to a proportion of from about 0.5 to 5.0% by weight of the mixture or composition that is to be polymerized.

Further additives B may also be mixed in with the compositions of the invention, these further additives including compounds which are incorporated non-covalently into the polymeric network. Such compounds may include, for example, commercially obtainable nematic liquid crystals.

Further possible additives B are pigments, dyes and fillers.

The pigments can be inorganic compounds, for example iron oxides, titanium oxide and carbon black. On the organic side suitable compounds are, for example, pigments or dyes from the class of the monoazo pigments, monoazo dyes and their metal salts, disazo pigments, condensed disazo pigments, isoindoline derivatives, derivatives of naphthalene- or perylenetetracarboxylic acid, anthraquinone pigments, thioindigo derivatives, azomethine derivatives, quinacridones, dioxazines, pyrazoloquinazolones, phthalocyanine pigments or basic dyes, such as triarylmethane dyes, and salts thereof.

Also suitable are special-effect pigments, such as aluminum or mica flakes, or pigments such as the pearlescent (pearl luster) and special-effect pigments obtainable commercially under the names Iriodin<sup>®</sup> and Paliocrom<sup>®</sup>, for example.

It is also possible to add customary fillers such as chalk, talc, gypsum and barytes, etc.

If the novel compositions have added to them as additives B the above-described crosslinkers and/or monomers and/or one or more of the chiral compounds likewise described above, then the latter are present in a proportion of from 0.001 to 50%, preferably from 0.01 to 20% and, with particular preference, from 0.1 to 10%, in

each case by weight. The proportion of crosslinkers and/or monomers is from 5 to 50% by weight, preferably from 10 to 20% by weight, with the sum of the proportions of the liquid-crystalline compounds, the crosslinkers and/or monomers and the chiral compounds of course having to add up to 100% by weight, and with the proportions relating to the overall amount of the compositions thus obtained.

For the claimed articles described below use is made of novel compounds, mixtures or compositions in which, in at least one compound of the formula Ia, at least one of  $P^1$  and  $P^2$  is a reactive radical. For simplicity these compounds, mixtures or compositions may be referred to as "polymerizable (novel) compounds, mixtures or compositions".

Claimed in accordance with the invention, therefore, is a process for printing articles or producing coatings having a liquid-crystalline order state on articles, which comprises applying to the articles polymerizable, novel compounds, mixtures or compositions, bringing about an orientation, if desired, and then polymerizing the compounds, mixtures or compositions applied to the articles.

Further suitable procedures for coating substrates or articles can be found, for example, in the document WO 96/02597.

The liquid-crystalline orientation comes about either spontaneously in the course of application or is achieved by known physical methods such as, for example, knife coating or the application of an electrical or magnetic field.

Considering, for example, the use of the polymerizable, novel compounds, mixtures or compositions in the field of screen printing or flexographic printing, their viscosity can be reduced by adding diluents. Apart from the use of rheological auxiliaries and additives with a similar action, a further possibility to influence the viscosities of the liquid-crystalline compounds, mixtures or compositions is to prepare mixtures of those compounds which differ in the number of the nuclei of their mesogenic groups M.

For example, mixtures of liquid-crystalline compounds having "trinuclear" and "dinuclear" mesogenic groups M, depending on their proportion, show a more or less reduced viscosity relative to the pure "trinuclear" compound or to a mixture of "trinuclear" compounds (explanations have already been given at the outset

regarding the "nuclei" of the mesogenic groups M). The converse of course is that it is possible to a greater or lesser extent to raise the viscosity of, for example, "dinuclear" compounds or mixtures thereof by the presence of appropriate amounts of

5 "trinuclear" or higher "polynuclear" liquid-crystalline compounds. Higher viscosities are desirable, for instance, in the field of offset and letterpress printing.

Also claimed, furthermore, are articles obtainable by printing or

10 coating by means of the abovementioned novel process.

The claims of the invention extend to the use of the polymerizable, novel compounds, mixtures or compositions for producing optical components, for example polarizing color

15 filters, especially notch filters, ie. narrow-band interference filters, or polarizers for LCD displays, and to their use for preparing liquid-crystalline colorants used, for example, in printing or in automotive finishing.

20 Additionally claimed in accordance with the invention are liquid-crystalline colorants which comprise polymerizable, novel compounds, mixtures or compositions.

25 With a view toward low-solvent formulations which are thus, inter alia, more friendly to the environment and user, there is increasing use of emulsions and dispersions. These generally have much lower viscosities than conventional formulations and are therefore of particular advantage from the standpoint of spray

30 coating techniques.

Consequently, aqueous emulsions or dispersions are also claimed which comprise polymerizable, novel compounds, mixtures or compositions and further auxiliaries customarily used to prepare

35 emulsions or dispersions. The preparation of dispersions comprising, inter alia, liquid-crystalline compounds is set out, for example, in the document WO 96/02597 and can be transferred analogously to the emulsions and dispersions claimed herein.

40 The novel aqueous emulsions and dispersions may if desired comprise not only the liquid-crystalline compounds and any further additives B, such as the abovementioned chiral compounds, monomers (crosslinkers), pigments, dyes, fillers, processing

45 auxiliaries or photoinitiators, but also, if desired, other auxiliaries such as light stabilizers and preservatives, for example. The content of polymerizable, novel compounds, mixtures or compositions in the novel aqueous emulsion or dispersions,

which are also suitable for use as interior and exterior paints, is generally from 20 to 95% by weight.

5 The addition of emulsifiers and/or dispersants as further auxiliaries is of particular importance.

10 As such auxiliaries it is preferred to employ water-soluble, high molecular mass organic compounds having polar groups, such as polyvinylpyrrolidone, copolymers of vinyl propionate or vinyl acetate and vinylpyrrolidone, partially hydrolyzed copolymers of an acrylic ester and acrylonitrile, polyvinyl alcohols with varying contents of residual acetate, cellulose ethers, gelatins or mixtures of these substances. Particularly preferred  
15 emulsifiers and/or dispersants with a function as protective colloids are polyvinyl alcohol having a residual acetate content of below 35, in particular from 5 to 30 mol percent and/or a vinylpyrrolidone-vinyl propionate copolymer having a vinyl ester content of below 35, in particular from 5 to 30 percent by  
20 weight.

Both nonionic and, in special cases, ionic emulsifiers/dispersants can be used. Preferred dispersants are relatively long-chain alcohols or phenols with different degrees  
25 of ethoxylation and/or propoxylation (adducts of from 4 to 50 mol of ethylene oxide and/or propylene oxide). Combinations of the abovementioned protective colloids with such emulsifiers/dispersants are particularly advantageous, since they give very fine emulsions/dispersions.

30 Further suitable emulsifiers/dispersants are, for example, dihexylsulfosuccinate, sulfosuccinate monoesters, the sodium salts of dodecylbenzenesulfonic acid and of pentadecanesulfonic acid, potassium oleate, sodium lauryl sulfate, alkyl  
35 polyglycosides, isooctylphenol, isononylphenol, C<sub>12</sub>-C<sub>18</sub> fatty alcohols and fatty alcohol alkoxylates.

Of particular suitability, furthermore, are polysiloxane-based emulsifying/dispersing auxiliaries.  
40

The emulsifying/dispersing auxiliaries described are suitable for preparing oil-in-water emulsions. It is, however, also possible to prepare emulsions or dispersions based on water-in-oil  
45 emulsions. Particularly suitable such emulsions or dispersions are emulsifiers and emulsifier mixtures as described, for example, in EP-A 0 623 630. Further suitable emulsifying/dispersing auxiliaries are sorbitan monostearate,



sorbitan monopalmitate, sorbitan tristearate, sorbitan monooleate, sorbitan esquioleate, polyoxyethylene sorbitol ethers, polyoxyethylene cetyl ethers, polyoxyethylene stearyl ethers and polyoxyethylene oleyl ethers.

5

The novel emulsions can also be miniemulsions. Miniemulsions have the advantage of forming particularly stable emulsions and are therefore especially stable on storage. To prepare miniemulsions, the above-described emulsions, which typically have droplet diameters in the micrometer range, are for example homogenized with the aid of a high-pressure homogenizer. This produces emulsions having droplet diameters in the range of a few hundred nm, in which no phase separation is seen for many weeks.

15

To prepare the novel dispersions or emulsions the novel compounds, mixtures or compositions are mixed, if desired, with a small amount of a solvent such as tetrahydrofuran, dioxane, acetone, methyl ethyl ketone, propanols, butanols, ethyl acetate, butyl acetate, methylene chloride, the xylenes or toluene, or else water, in order to reduce the viscosity. Preferably, however, said polymerizable, novel compounds, mixtures or compositions are admixed directly with the emulsifying/dispersing auxiliary, which can also be added as an aqueous solution. The resulting mixture is thoroughly homogenized by means, for example, of stirring. Then water is added and thorough homogenization is repeated. The amount of water is guided by the desired use. It is preferred to add from 20 to 80% by weight, with particular preference from 40 to 60% by weight, of water based on the overall amount of the finished emulsion or dispersion. For processing purposes the emulsions/dispersions can be diluted to the desired viscosity and colorant concentration with water to which, in turn, an emulsifying/dispersing auxiliary may be added.

35

Possible methods of curing the films formed from the emulsion/dispersion are, as for the coating mixtures, thermal methods or radiation methods, such as photocuring or electron beam curing, depending on the nature of the polymerizable groups. The addition of polymerization initiators, as described for the coating mixtures, is also advantageous for the curable dispersion films.

The advantage of the dispersion coatings lies in the ease of processing. The dispersions have low viscosities, can be prepared without solvent and thus require no ventilation equipment, and can be applied by all known, simple techniques such as spreading,

45

rolling, spraying, printing, dipping or curtain coating. In accordance with the novel coating process, spontaneous orientation takes place even from the dispersion, so that in the presence of appropriate additives such as chiral compounds it is possible for a desired, perceived color, which is dependent on the viewing angle, to be formed.

Also claimed are pigments obtainable by polymerizing, as a thin film on a substrate, the polymerizable, novel compounds, mixtures or compositions, detaching the polymeric mass from the substrate and comminuting it to pigment particle size.

The film thicknesses are chosen during preparation such that the finished pigment particles have thicknesses of from 0.5 to 50  $\mu\text{m}$ , preferably from 1 to 25  $\mu\text{m}$ , and, with particular preference, from 2 to 10  $\mu\text{m}$ . The mean diameters of the pigment particles are at levels corresponding to from 3 to 100 times the thickness of the pigment particles; in other words, the ratio of mean diameter to thickness of the pigment particles is from 3:1 to 100:1. Preference is given to a ratio of from 4:1 to 25:1, with particular preference from 5:1 to 15:1. In this context the film can be applied, for example, by using a doctor blade. Typical gap widths in this case are from 7.5 to 400  $\mu\text{m}$ .

By means of casting techniques which are customary, for example, in the production of magnetic tapes it is possible to establish film thicknesses of a few  $\mu\text{m}$ . Depending on which volatile additives are present in which amounts in the course of film production, the thicknesses in the finished pigment particles will then be greater or lesser fractions of these wet film thicknesses.

It is advantageous if appropriate procedures are used, even before polymerization, to determine the dimensions and form of the products present after polymerization. The losses occurring by subsequent comminution and classification of the polymer products, especially as a result of the production of excessively fine material, can in this way be largely avoided.

Particular preference is therefore given to pigments which are obtainable by applying polymerizable, novel compounds, mixtures or compositions by printing to a substrate, the printing process predetermining the subsequent pigment form and pigment dimensions, subjecting said compounds, mixtures or compositions to polymerization, and then detaching the polymer products from

the substrate. With regard to the pigment dimensions, what has already been said above applies here too.

Procedures for producing appropriately shaped pigments are described, for example, in the prior German applications 196 02 795.0 and 196 02 848.5.

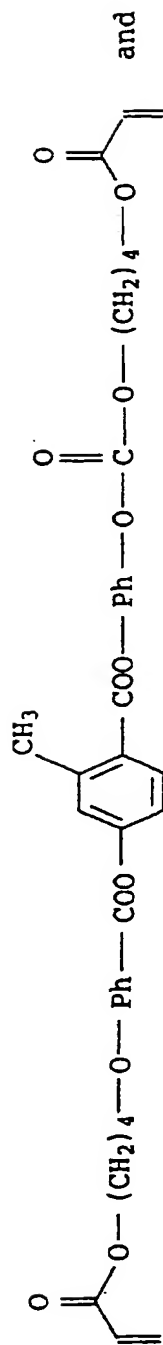
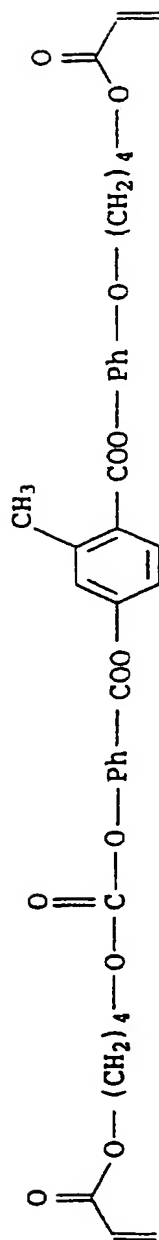
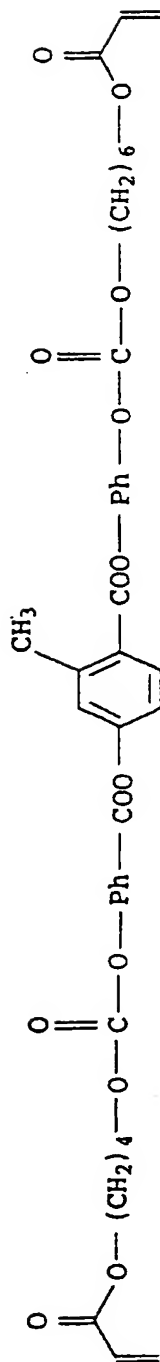
The pigments obtainable in accordance with the invention can be employed not only in conventional coating materials but also in waterborne coating materials. Examples of those formulations in which the novel pigments can be employed as special-effect pigments are set out in the documents WO 95/29961 and WO 95/29962.

#### 15 Preparation Examples

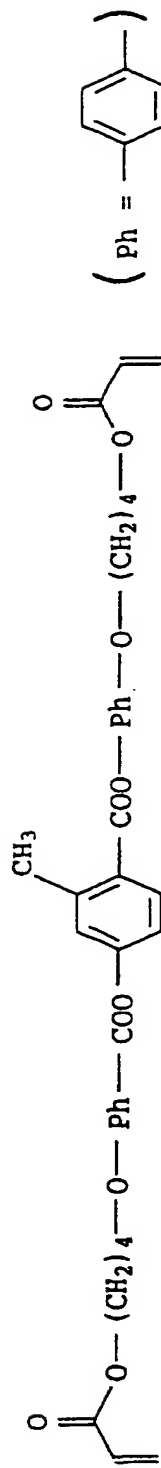
##### Example 1

20 49.4 g (0.133 mol) of bis-1,4-(p-hydroxybenzoic acid) methylphenylene diester, 22.2 g (0.133 mol) of chlorobutyl acrylate, 20.2 g (0.15 mol) of potassium carbonate (ground), 0.2 g of potassium iodide, 0.05% of Kerobit<sup>®</sup> BHT and 0.01% of 4-hydroxy-TEMPO (obtainable commercially from Hüls) were stirred  
25 in 250 ml of DMF at 80°C under nitrogen for 5 h. The mixture was cooled to room temperature. Then 38.3 ml (0.255 mol) of N,N-dimethylcyclohexylamine and 38.5 g (0.186 mol) of acryloylbutyl chloroformate were added dropwise. Finally, the reaction mixture was stirred at 40°C for a further 3 h. Following  
30 the addition of 500 ml of ethyl acetate, inorganic residues were filtered off with suction and the organic phase was extracted with dilute hydrochloric acid and then with water. The organic phase was dried over sodium sulfate, filtered and concentrated to give 83 g of product, corresponding to a yield of 94.5%.  
35

The resulting mixture contains the compounds



and

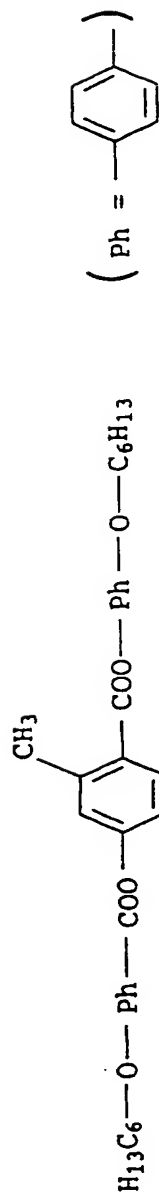
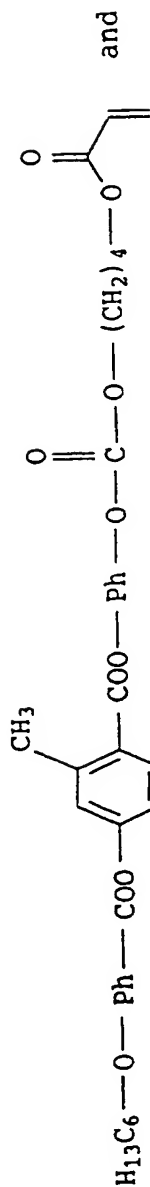
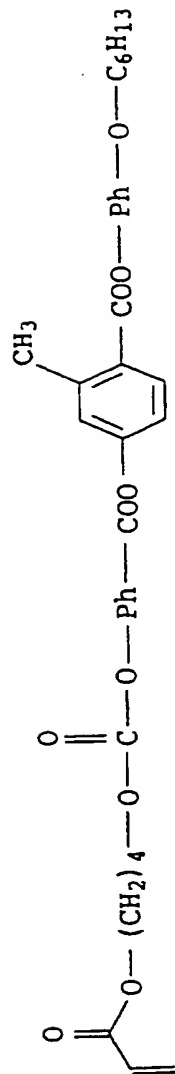
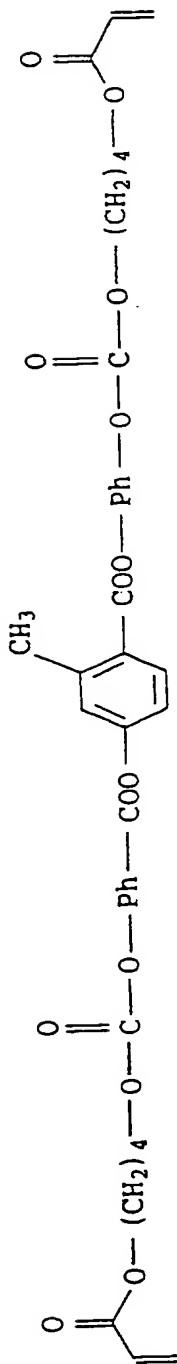


in a molar ratio of approximately 1:1:1:1.

The phase behavior of the mixture is n 117-125 i; in other words, the mixture is nematic (n) liquid-crystalline to 117°C and within the range from 117 to 125°C (the two-phase region) goes into an isotropic phase (i). Above 125°C, only the isotropic phase is still present.

## Example 2

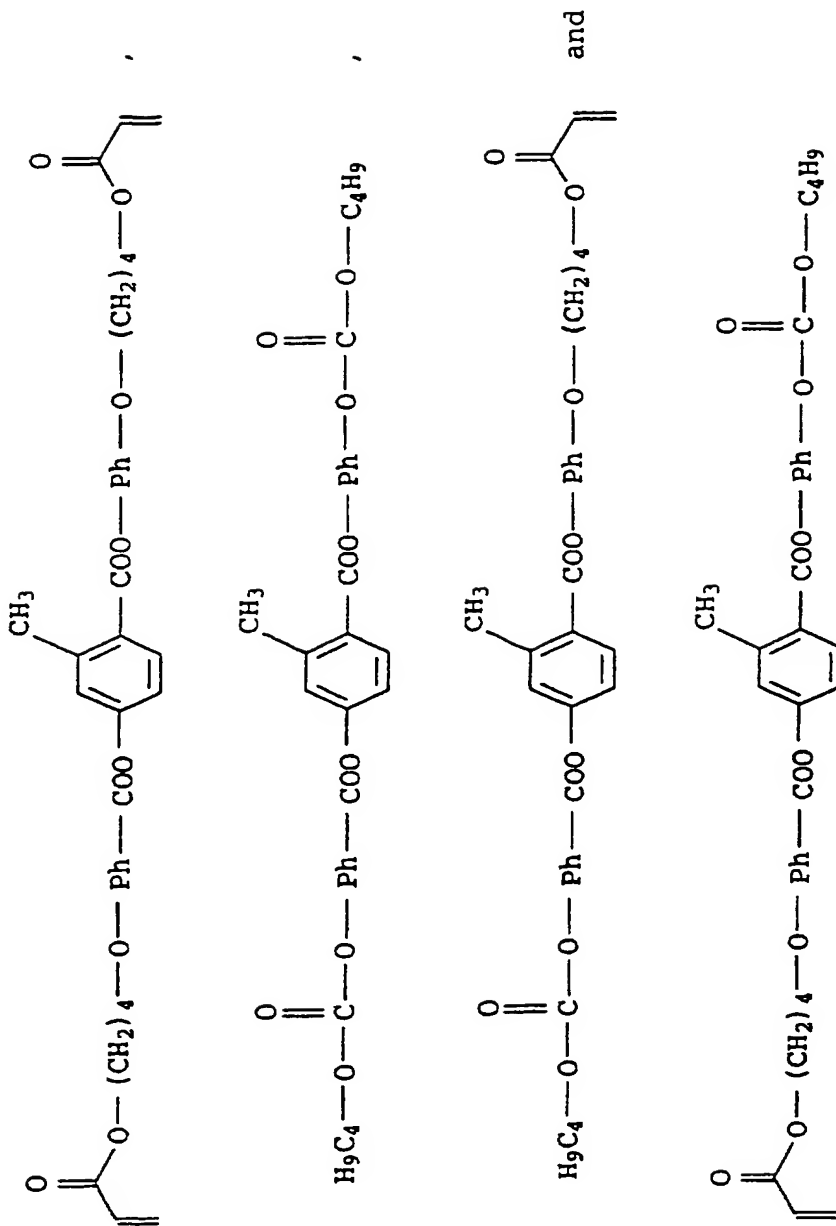
The procedure of Example 1 was repeated but using the corresponding molar amount of bromohexane instead of the chlorobutyl acrylate. The resulting mixture contains the compounds



in a molar ratio of approximately 1:1:1:1. The phase behavior of the mixture is n 131-138 i.

## Example 3

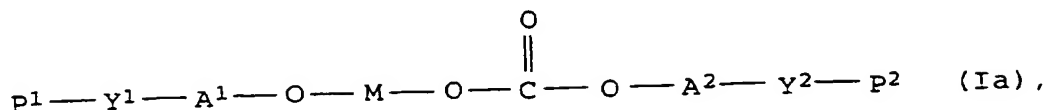
The procedure of Example 1 was repeated but using the corresponding molar amount of butyl chloroformate instead of the acryloylbutyl chloroformate. The resulting mixture contains the compounds



in a molar ratio of approximately 1:1:1:1. The phase behavior of the mixture is n 131-141 i.

Claims

- 5 1. A liquid-crystalline compound of the formula Ia



10

where

15  $p_1$  and  $p_2$  each independently are hydrogen,  $C_1$ - $C_4$ -alkyl or reactive radicals by means of which polymerization can be brought about,

20  $y_1$  and  $y_2$  each independently are a single chemical bond, oxygen, sulfur,  $-O-CO-$ ,  $-CO-O-$ ,  $-O-CO-O-$ ,  $-CO-NR-$ ,  $-NR-CO-$ ,  $-O-CO-NR-$ ,  $-NR-CO-O-$  or  $-NR-CO-NR-$ ,

20

R is hydrogen or  $C_1$ - $C_4$ -alkyl,

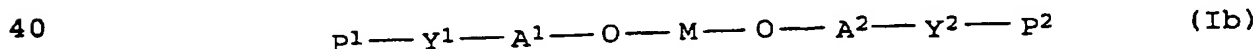
25  $A^1$  and  $A^2$  are spacers having one to 30 carbons in a chain which can be interrupted by oxygen in ether function, sulfur in thioether function or by nonadjacent imino or  $C_1$ - $C_4$ -alkylimino groups, and

30 M is a mesogenic group.

2. A mixture comprising

35  $(A_1)$  one or more liquid-crystalline compounds of the formula Ia as claimed in claim 1,

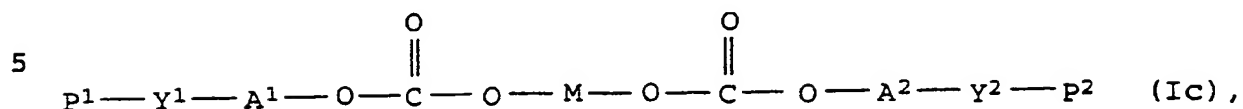
$(A_2)$  if desired, one or more liquid-crystalline compounds of the formula Ib



and/or

45

(A<sub>3</sub>) if desired, one or more liquid-crystalline compounds of the formula Ic

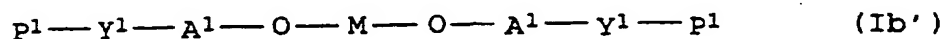


where p<sup>1</sup>, p<sup>2</sup>, y<sup>1</sup>, y<sup>2</sup>, A<sup>1</sup>, A<sup>2</sup> and M in the formulae Ib and Ic are each as defined in formula Ia but in specific individual cases their selection is independent for the compounds Ia, Ib and Ic.

3. A mixture comprising

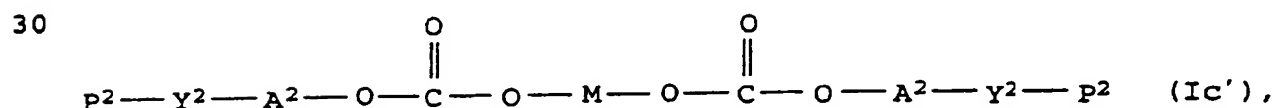
(A<sub>1</sub>') one or more liquid-crystalline compounds of the formula Ia as claimed in claim 1,

(A<sub>2</sub>') one or more liquid-crystalline compounds of the formula Ib'



and

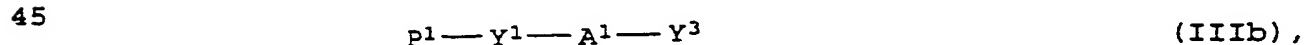
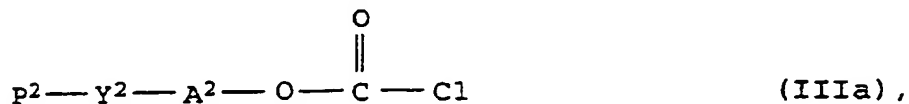
(A<sub>3</sub>') one or more liquid-crystalline compounds of the formula Ic'



obtainable by reacting one or more compounds of the formula II



with one or more compounds of the formulae IIIa and IIIb





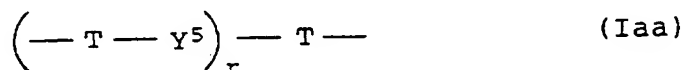
where  $p^1$ ,  $p^2$ ,  $y^1$ ,  $y^2$ ,  $A^1$ ,  $A^2$  and  $M$  are as defined in claim 1 and  $Y^3$  is a leaving group: " " "

4. A composition comprising

(A) a compound or mixture as claimed in any of claims 1, 2 and 3, and

(B) one or more further additives.

5. A compound, mixture or composition as claimed in any of claims 1 to 4, in which  $M$  is a mesogenic group of the formula Iaa



where:

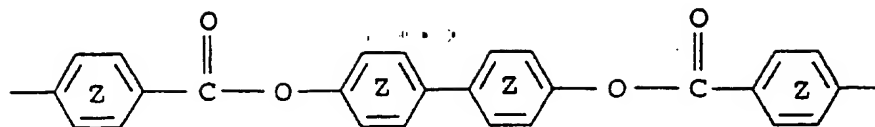
$T$  at each occurrence is a divalent, saturated or unsaturated, isocyclic or heterocyclic radical,

$Y^5$  at each occurrence is a group as defined for  $Y^1$  and  $Y^2$  or is  $-O-CH_2-$ ,  $-CH_2-O-$ ,  $-CH=N-$ ,  $-N=CH-$  or  $-N=N-$  and

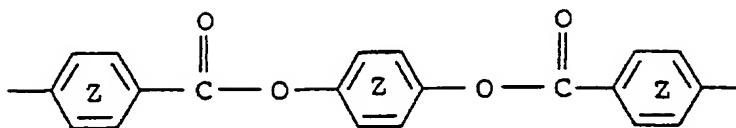
$r$  is 0, 1, 2 or 3,

and, if  $r > 0$ , both  $T$  and  $Y^5$  are identical or different at each occurrence.

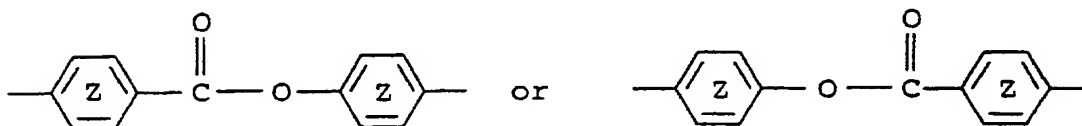
6. A compound, mixture or composition as claimed in any of claims 1 to 4, in which  $M$  is a mesogenic group selected from the following formulae



5



10



where each ring Z can carry up to three identical or different substituents from the following group:

15

hydrogen, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>20</sub>-alkoxy, C<sub>1</sub>-C<sub>20</sub>-alkoxycarbonyl, C<sub>1</sub>-C<sub>20</sub>-monoalkylaminocarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyl, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonyloxy, C<sub>1</sub>-C<sub>20</sub>-alkylcarbonylamino, formyl, carboxyl, halogen, cyano, hydroxyl and nitro.

20

7. A compound, mixture or composition as claimed in any of claims 1 to 6, in which, in at least one compound of the formula Ia, at least one of P<sup>1</sup> and P<sup>2</sup> is a reactive radical.

25

8. A process for printing articles or producing coatings having a liquid-crystalline order state on articles, which comprises applying to the articles a compound, mixture or composition as claimed in claim 7, bringing about an orientation, if desired, and then polymerizing the compound, mixture or composition applied to the articles.

30

9. A printed or coated article obtainable by a process as claimed in claim 8.

35

10. The use of a compound, mixture or composition as claimed in claim 7 for producing optical components.

40

11. The use of a compound, mixture or composition as claimed in claim 7 for preparing liquid-crystalline colorants.

12. A liquid-crystalline colorant comprising a compound, mixture or composition as claimed in claim 7.

45

13. An aqueous emulsion or dispersion comprising a compound, mixture or composition as claimed in claim 7 and further auxiliaries commonly used to prepare emulsions or dispersions.

5

14. A pigment obtainable by subjecting a compound, mixture or composition as claimed in claim 7, as a thin film on a substrate, to polymerization, detaching the polymeric mass from the substrate and comminuting it to pigment particle size.

10

15. A pigment obtainable by applying a liquid-crystalline compound, mixture or composition as claimed in claim 7 by printing to a substrate, the printing process predetermining the subsequent pigment form and pigment dimensions, subjecting said compound, mixture or composition to polymerization, and then detaching the polymer products from the substrate.

15

- 20 16. A liquid crystalline compound, mixture or composition as claimed in any of claims 1 to 7 and substantially as hereinbefore described or exemplified in any of the foregoing Examples.

25

30

35

40

45



Application No: GB 9818019.3  
Claims searched: 1-16

Examiner: Peter Davey  
Date of search: 5 November 1998

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.P): C2C (CYT), C4X  
Int Cl (Ed.6): C07C 69/96, C09K 19/20  
Other: Online: WPI, CAS ONLINE

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WO 97/00600 A1 (BASF), see eg. page 11, line 30; page 14, line 25; and page 31, line 5	1 at least
X	Chemical Abstracts 83:106737 and JP 49045149 B4 (MITSUBISHI ELECTRIC), see compound with Registry No. 33926-48-6	1 at least
X	Chemical Abstracts 82:178983 and JP 49037352 B4 (HATTORI ET AL), see compound with Registry No. 55290-82-9	1 at least
X	Chemical Abstracts 75:41754, see compounds with Registry Nos. 33926-37-3 and 33926-25-9	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**